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PHYSICAL SCIENCES

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Volume 8

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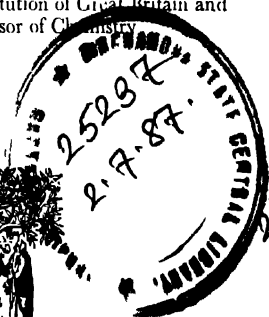
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Friday, January 21, 1916.

HIS GRACE THE DUKE OF NORTHUMBERLAND, P.C., K.G., LL.D.,
F.R.S., President, in the Chair.

PROFESSOR SIR JAMES DEWAR, M.A., LL.D., D.Sc., F.R.S., M.R.I.,
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Problems in Capillarity.

STUDIES in gas diffusion described in last year's discourse have lead to the examination of films of great tenuity for such enquiries. These films can be got in the solid state through the use of solutions of nitro-cotton in certain solvents, or in the liquid state by employing Plateau's soap solution. The object of the present Discourse is to describe the result of some attempts to produce apparatus suitable for the study of the properties of such films, along with an account of the results so far obtained.

Liquid films thin enough to show colours are produced when drops of a large number of organic substances are allowed to touch the surface of pure water. The apparatus adapted for demonstrating the colour bands and also for making solid films is shown in Fig. 1. A copper funnel A of 10 cm. diameter, blackened by coating with nitrate of copper and subsequent heating to redness, is connected to the Institution water supply in order to obtain an easily renewable and well-defined clean water surface. The funnel is fixed in a blackened hollow metal conical stand B shown in section; this stands on a shelf over a sink. A parallel beam of light is directed down at about 40° inclination, and, after reflection from the liquid surface in the funnel, is focused on the screen. The best definition is obtained by allowing the water surface to fall a little below the rim of the funnel, for which purpose a two-way tap is connected below. It is essential that a fresh surface be produced by flooding with water between each experiment. A small drop of a suitable liquid on the end of a glass rod is made to touch the water in the funnel near the centre of the surface. The difference of surface tension between the water and the liquid drop results in the latter being spread to a circular film thin enough to produce colour bands in the same definite order exhibited by soap films. The production and development of the colouring is generally very rapid, so that the final thinnest stage of blackness is quickly reached. Pinene, turpentine,

chlor-benzene, tetra-hydro-quinoline and olive oil are a set of bodies that show marked contrasts.

SOLID COLLODION FILMS.

A solution of nitrated cotton can be readily made in amyl acetate. If a drop of this solution is allowed to touch the water

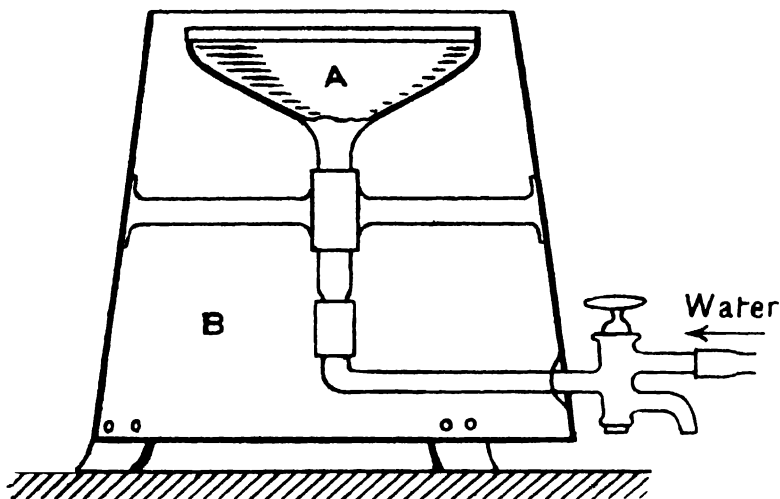


FIG. 1.

surface, a circular film showing the rings of colour steadily spreads out. The amyl acetate quickly evaporates, as shown by the regular disappearance of the colours, and an extremely thin black solid film of the nitro-cotton is left. This can be folded over, showing the stages of colour produced by increasing thickness. If a flat ring support is carefully slipped under the film it can, by careful handling, be completely removed by a drawing motion at a steadily increasing elevation. Black films 15 cm. in diameter can be so obtained. They are easily dried, and quite permanent with careful handling. They can be weighed, and their thickness thereby estimated. For example, the mean weight of several films 11 cm. in diameter was found to be 0.432 mgms.; the density of the collodion cotton being 1.60, it follows that the thickness of the black film, if uniform, will be of the order of 3×10^{-6} cm., i.e. 30 μ . The average thickness of a film can also be found by knowing the weight of a drop of a collodion solution in a known concentration, and

subsequently increasing the diameter of the large circular film produced.

For studying the transit of gases films about 5 mm. in diameter were used. They were mounted on a thick-walled glass tube ground flat and polished at one end. The tube was fixed vertically and centrally under the water surface before making the film. The water is afterwards allowed to flow slowly out, carrying the film down, thereby folding it securely and neatly over the ground end of the tube. The water level inside and outside the tube must be kept the same by a suitable air inlet, otherwise the suction may break the film. By this means two, three or more black films can be overlaid, and different coloured films obtained.

In order to investigate the passage of air through such films a small pressure was introduced into the tube supporting the film, and the diminution with time measured on a sensitive alcohol displacement manometer. A soap bubble was used to supply a small regulated pressure.

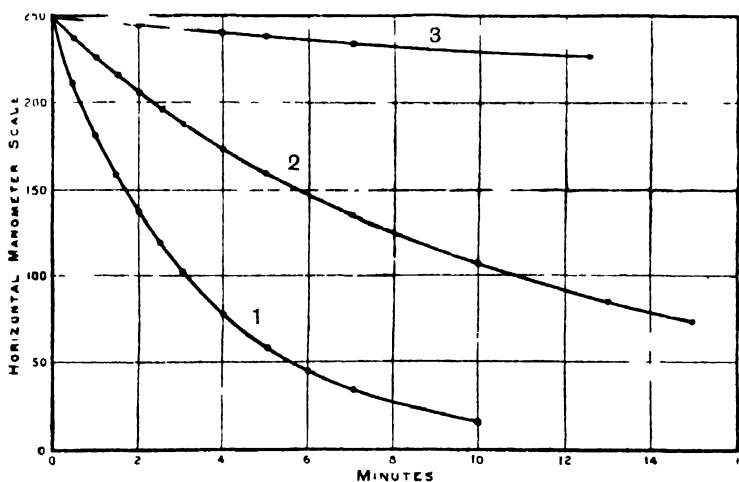


FIG. 2.

The above graph (Fig. 2) shows the observed fall of pressure (p) as ordinates, with time (t) as abscissæ, got from observations from three separate films freshly dried in a warm oven before measurement.

(Curve No. 1 is the graph of one film. Nos. 2 and 3 of a double and triple film. In all cases the fall of pressure was logarithmic. That is to say, when $\log p$ is plotted with t a straight line graph is

obtained; from whence we deduce that the rate of diminution of pressure is proportional to the pressure.

The actual quantities dealt with in a typical instance are as follows. 50 mm. of the alcohol manometer scale are equivalent to 1 mm. water pressure:—

Observations of pressure with time were:

P (mm. H ₂ O)	4.4	3.15	2.4	1.81	0.82	0.44
t (minutes)	0	$\frac{1}{2}$	1	2	3	4

Volume of enclosed space = 30 c.c.

Area of membrane = 0.049 sq. cm. (0.25 cm. diameter).

Fall of pressure in first $\frac{1}{2}$ minute = 1.25 mm. water = 0.00012 atmosphere.

∴ Volume of air passed in first $\frac{1}{2}$ minute = $30 \times 0.00012 = 0.0036$ c.c.
= 10.45 cc. per day.

∴ Volume passed through 1 sq. cm. in 1 day = $\frac{10.45}{0.049} = 209$ c.c.

The mean water pressure during experiment was 3.8 mm., or 0.00037 atmosphere.

On the assumption that the rate of diffusion remains proportional to the pressure up to one atmosphere, then the extrapolated value of the rate per sq. cm. per day at atmospheric pressure would be 565 litres.

A similar determination from the fall of pressure in the second whole minute gives a value of 930 c.c. per day per sq. cm. at a mean pressure of 1.86 mm. of water. If this be extrapolated to one atmosphere, the rate per sq. cm. becomes 520 litres.

Compared with this, the rubber membrane 0.001 cm. thick had a rate of 2 c.c. of air per sq. cm. per day. The mean thickness of the black collodion film is 0.000003 cm. or $\frac{3}{1000000}$ ths of the rubber. The rate of air transit through the collodion at one atmosphere appears thus to be 260,000 times that of rubber. The square of the ratio of the thicknesses is roughly of the same order as the inverse ratio of the diffusion rates.

The corresponding extrapolated values at one atmosphere were 592 for a single black film, 36 for the double film (whose colour appeared very pale golden), and just under 1 for the triple film (reflecting a brown-magenta colour). The extraordinary diminution of gas percolation thus observed is very remarkable.

COLLODION FILMS: MICROSCOPIC EXAMINATION.

A microscopic examination seems to throw some light on this question of gas transit. A regular distribution of minute bubbles is revealed, which occur largely in colonies composed of one or two larger bubbles with ten or twenty very small ones surrounding them like small patches of froth. These patches seldom exceed 0.025 mm.

in width; the larger bubbles are not often over 0.008 mm. diam. The appearance of the colonies are roughly represented in Fig. 3.

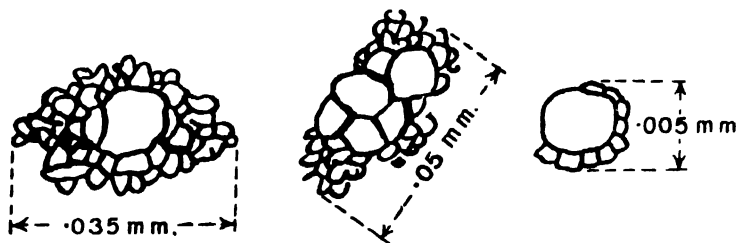


FIG. 3.

Between the fairly equally spaced colonies there was a regular distribution of smaller bubbles of from 0.005 to 0.001 mm. Among these a small proportion were colonies, but of a low order of aggregation.

In one straight line of length, 1.53 mm. across a film, there were: -

10 colonies of from 0.01 to 0.02 mm. ...	Total = 0.15)
15 " " 0.005 " 0.01 " ...	" = 0.11
about 50 " about 0.001 " 0.003 " ...	" = 0.10)

0.36 mm.

The proportionate length of bubbles = 0.36 mm. in 1.53 mm. of film, or $23\frac{1}{2}$ per cent, so that the total relative area of bubbles to continuous film - $(0.235)^2 = 0.055$, or $5\frac{1}{2}$ per cent.

The appearance of double and triple films under the microscope was simply that of a more thickly sown appearance of the bubbles. One perfectly black film $1\frac{1}{2}$ cm. diam. showed much smaller bubbles, and much more thinly spread; the most numerous were 0.004 mm. diam. In a slightly thicker film the bubbles are somewhat larger.

From the dimensions of these bubbles and colonies it is evident that they must be very flattened in shape in the film, because its thickness is at most one-hundredth of the length of the bubbles. The upper and lower bounding surfaces of these bubbles must, therefore, be extremely thin relatively to the mean film thickness. This suggests that the main diffusion most likely occurs through these extremely thin portions of the film. When two films are superposed, the bubbles will not be likely to coincide to any great extent, as they only occupy about $5\frac{1}{2}$ per cent of each film. The exaggerated diffusion through the thin places will thus be largely checked. The addition of a third film would further reduce this by a similar factor,

so that the diffusion would diminish fairly geometrically. In the example given above the relative rate of the double film was $\frac{1}{17}$ th that of the single film, while the addition of a third film again reduced this by $\frac{1}{36}$ th.

If these bubbles were actual holes, then the gas transit would be that of simple transpiration. This would give a curve of an entirely different character to those shown in Fig. 2. The plots of $\log. p$ and t would no longer give a straight line, as the rate of gas transit is then proportional to the square root of the pressure. This was actually tried on a capillary tube, when the appropriate curve of diminution of pressure with time was obtained.

The bursting pressure of a collodion black film of double thickness was found by connecting the open end of the polished glass tube on which it was mounted, as described above, to a mercury manometer. Air pressure was gently introduced, and the height of the mercury pressure required to burst the film observed. As an example, a film of double thickness, $3\frac{1}{2}$ mm. in diam., burst at 3 cm. pressure of mercury, corresponding to a load of 40 grms. weight per sq. cm.

SOAP FILMS IN EXHAUSTED VESSELS.

Films of soap solution can readily be obtained of the same order of thickness as those from collodion. When produced in exhausted vessels they are freed from many disturbing agencies. The deleterious effects of suspended matter and other air impurities are avoided; convection currents and air friction disappear; and the motions in the film are rendered more definite. The solution being free from dissolved gases, the absence of oxygen and carbonic acid stabilises the soap solution, which, however, may in time be damaged by attack on the glass. Any froth that may be produced rapidly subsides, because the bubbles are formed only of water vapour, which condenses quickly owing to the higher pressure inside the bubbles.

The three methods of film production in exhausted vessels most frequently used are:—

(a) Production of bubbles of water vapour from the slightly warmed soap solution, or by violently shaking the liquid until it becomes a mass of froth and allowing to stand.

(b) "Throwing" the film by a smooth and rapid circular swish of the soap solution over and round a constricted neck; or across a cylindrical vessel.

(c) Immersing, or otherwise covering, a wire or glass framework, which is thus left holding a film when the soap solution is carefully withdrawn from it.

The first method is applicable to an ordinary distilling flask, or plain exhausted tube, such as are shown in Fig. 4. The flask has a

capacity of about a litre, and the straight tube was about 60 cm. in length and 4 cm. in diameter. Both are sealed after exhausting to a fraction of a mm., the part containing the soap solution being meanwhile cooled to about -20°C . When the bulb A is then gently warmed on either side by the finger and thumb, a regular succession of bubbles rise from two opposite points of A, which are thus at a slightly higher temperature. The growing bubbles pass in their expansion to and fro across the liquid surface almost with

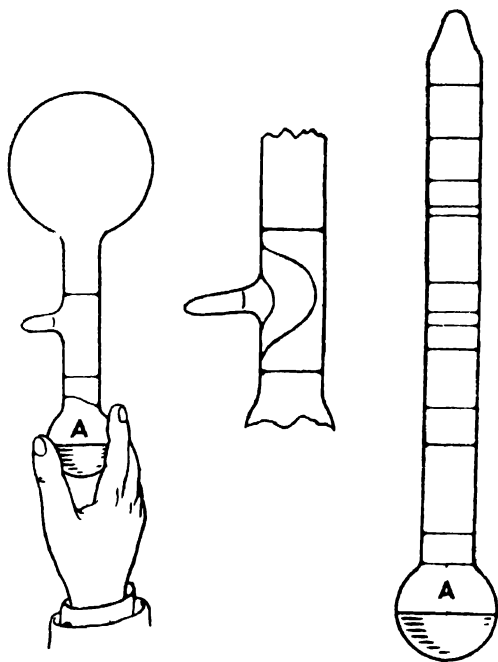


FIG. 4.

the regularity of a pendulum, and rise up the tube as a series of flat films. In a similar manner, if the side tube (filled with the solution) be warmed by the fingers, saddle-backed films emerge and divide into flat films up and down the straight neck (see Fig. 9). An alternative method more applicable to the straight tube form is to agitate the liquid until it is largely a mass of froth, the bulb A being warmed in the hand during the shaking. When the tube is then set vertical, the slight warmth imparted to the liquid mass in A causes a steady and extensive evolution of interlacing bubbles to

up the tube. These bubbles soon settle to a succession of flat films, thirty being frequently obtained in such a tube. The films thin down to the black stage in a few hours at most, and slowly descend in the tube during many days, provided the temperature

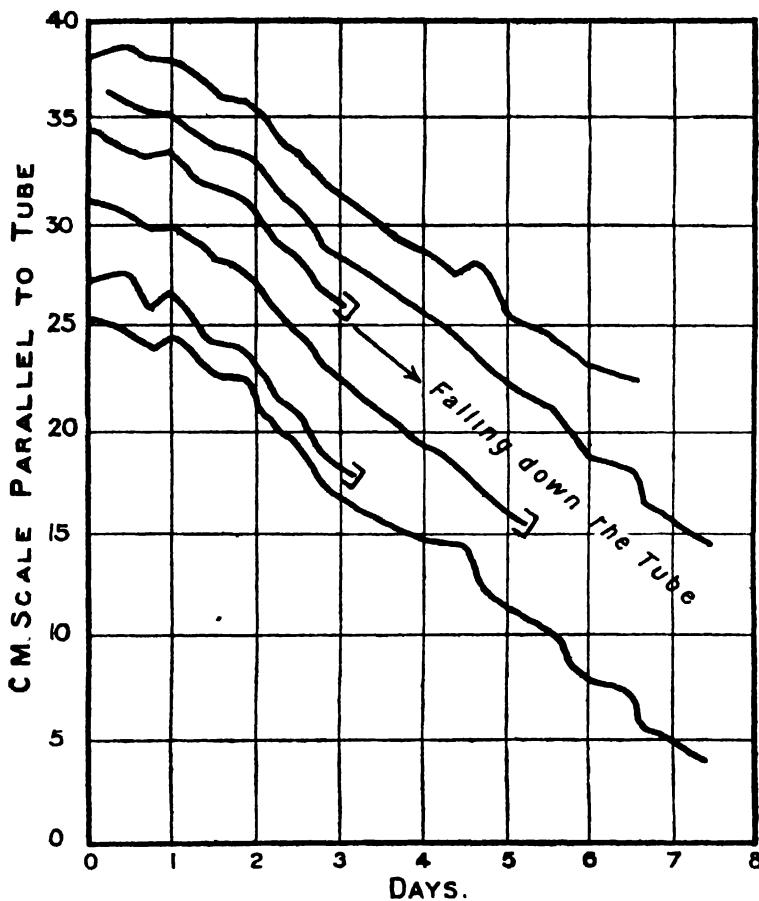


FIG. 5.

remains constant. They are instantly responsive to any slight alteration of temperature, being so sensitive that the approach of the hand is sufficient to cause movement, from the minute alteration of vapour pressure produced by the small increase of heat radiation.

If one film be broken, the remainder rearrange their positions, those nearest the disturbance being most affected.

Examination of the manner of the fall of the films in the tube shows that the rate is approximately steady through the greater part of the tube, when not too many films are present. As the films become more crowded in the lower part, the rate of fall decreases. If the tube is not strictly cylindrical, then, provided the narrower part is above, the films may either remain almost steady, or if the difference of diameter is sufficient, the films will steadily rise; they can thus indicate differences from uniformity of section, too small to be perceptible to the eye. In a similar way small irregularities or slight unevenness of surface are indicated by a proportionate distortion in the film itself from a perfect plane, because the film sets perpendicular to the supporting surface. Variations of temperature are indicated by an interruption to the smooth progress of the films through the tube. Thus, in a quiet room, where the temperature is falling, the mass of liquid will cool more slowly than the thin glass walls and supporting films; and a slight evolution of water vapour rising from the liquid will drive the films up the tube. Such variations are well shown in a graph of continuous records of such a set of films. (Fig. 5.)

The draining of the liquid from the tube walls is well exhibited by the steady decrease of thickness of the liquid rings of contact around each film. The interactions, in these films, of the surface tension and other forces, such as gravity, have been very thoroughly investigated by the American mathematician, Willard Gibbs, and this ring of contact is therefore appropriately termed the Gibbs ring or layer. It is seen that the films remain all black, i.e. of uniform thickness, while the various Gibb layers are variable according to the excess of liquid on the neighbouring glass surface. The amount of liquid they contain will vary from two or three times that present in the film up to a considerable amount. This relative amount can also be varied by small temperature variations imposed on the Gibb layer, which can cause a stream of liquid to pass out therefrom into the film which thereby becomes thickened. A similar result is obtained by differences of vapour pressure on the two sides of a film caused by small alterations of temperature, condensation on the film then taking place.

A special form of exhausted vessel constructed for the purpose of keeping the film stationary is shown in Fig. 6. It has two equal bulbs A and B with a slight, but rather sharp constriction between them, forming a neck on which the film is thrown. The two bulbs are drawn out on opposite sides of the neck to a tubular bend to form an enclosed space freely open to each side of the film, and the equality of pressure thus secured prevents the film from being disturbed by variations of vapour tension with temperature. A small bulbed reservoir is sealed in the centre of the tubular bend

on the side farthest from the double bulb. The diameters of the films so obtained were varied in the different vessels used from 1 to 8 cm. After filling with the requisite amount of liquid, the whole can be exhausted through the tubular extension of the reservoir. In order to obtain a film the liquid is tilted over into one of the

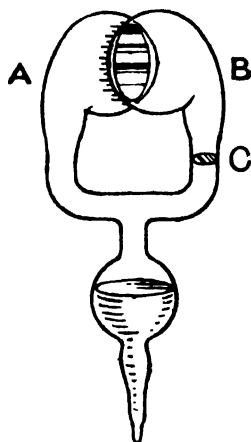


FIG. 6.

double bulbs and swirled with a single gentle sweeping motion round and over the neck, thus leaving a film across the opening. With a suitably shaped neck, provided there is a sufficient amount of liquid, very little practice is necessary. It may be added that films in the double bulb of Fig. 6 remain indefinitely. Even without any neck, a film can be obtained by practice in a plain cylindrical vessel of considerable diameter. One such film 19 cm. in diam. in a closed bottle is on the table, having become perfectly black since it was thrown more than a week ago.

The double bulbs have proved to be very convenient for systematic study of plane films, from the ease with which they can be manipulated. In addition to the film at the neck, other films across the tube as at C can be obtained. Such a film acts as a stopcock, isolating the opposite sides of the main film on the neck. This can then be subjected to slight differences of pressure by gentle warmth from the hand. Instead of a plane film varying degrees of curvature can be obtained. Many effects on the character and appearance of the films can thus be studied, and have proved interesting.

The illumination, either for direct visual study or projection, is easily arranged without much disturbance from the glass surfaces. A slightly condensed beam of light from an arc lamp, passing through

a plane-sided water cell to prevent heating, is directed at a moderate inclination on to the film, and the reflected light is focused on the screen by means of a suitable lens. For visual examination more diffuse lighting is preferable, and this can be obtained by placing a ground glass in the path of the incident beam at a little distance from the film, or for large films a plain white screen adjacent to the film should be suitably illuminated either by diffuse daylight, or beam from a lamp. In either case a black background must be provided to the film, to absorb the transmitted light.

With a smoothly blown bulb, very little distortion is produced, so that a clear elliptical image is seen. The appearance of the film at two stages of development is shown in the accompanying plate (Plate I.) A portable form is shown in Fig. 7. The bulb is mounted in a black box provided with a window opposite and parallel to the film. The window is central with the film of the same width, but

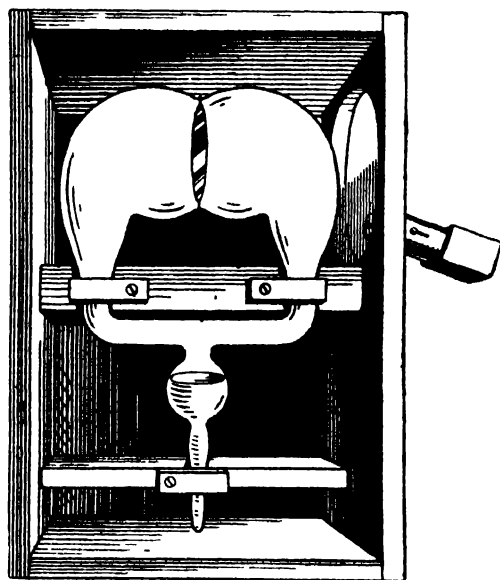


FIG. 7.

about twice the height. The lower half of the window is ground glass, illuminated by an ordinary electric pocket lamp fixed in a small box. The film is viewed through the upper clear part of the window.



PLATE I.



The main features of the colour grading to be seen in such a film, apart from the black stage which is obtained later, are two purple to blue bands, more or less wide and separated according to the amount of thinning which has occurred. A less distinct third band is a redder shade of purple and is not so strikingly contrasted. This banding is well adapted for showing the mobility of the film, as a freely moving disc of liquid. When rotated in its own plane, the thickest and heaviest part will of course remain at the bottom, while the remainder of the film will be relatively placed according to its decreasing mass, and the surface tension will retard any relative motion of the parts. The colour bands, therefore, will keep horizontal when the film bulb is rocked in the plane of the film. To show the movement, some uniformly spaced black and white bands are marked on a card surrounding the film and in the same plane (see Fig. 8). The card is fixed to the film bulb and moves with it when rocked,

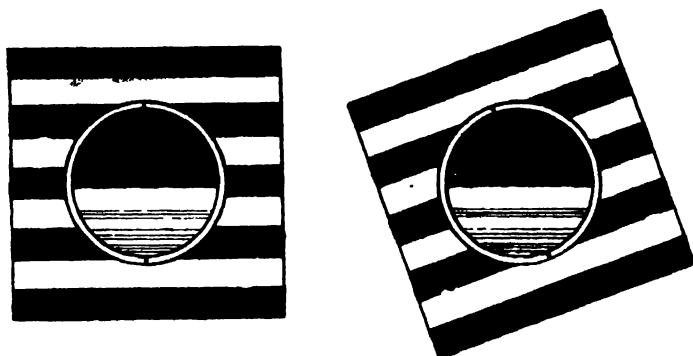


FIG. 8.

while the bands are seen to remain practically stationary. With a suitable scale replacing the banded card, the amount of displacement from the horizontal can be read. The film can thus be used as a level, and from its permanence and easy production finds a ready application to such a purpose. A half black film in which the lower half is too thick to show colour is a better index than the varying colour bands, and gives instead a bright contrast in a very mobile condition. This is readily obtained from the totally black film, usually found in a bulb which has been left for a short time. The liquid for providing the thicker uncoloured part comes from the excess present in the Gibb ring. A quick rocking motion or oscillation in the plane of the film soon causes enough of the excess liquid to be transferred to the film, and instead of becoming uniformly distributed, it steadily accumulates upwards over the black film to any desired amount. Finally, of

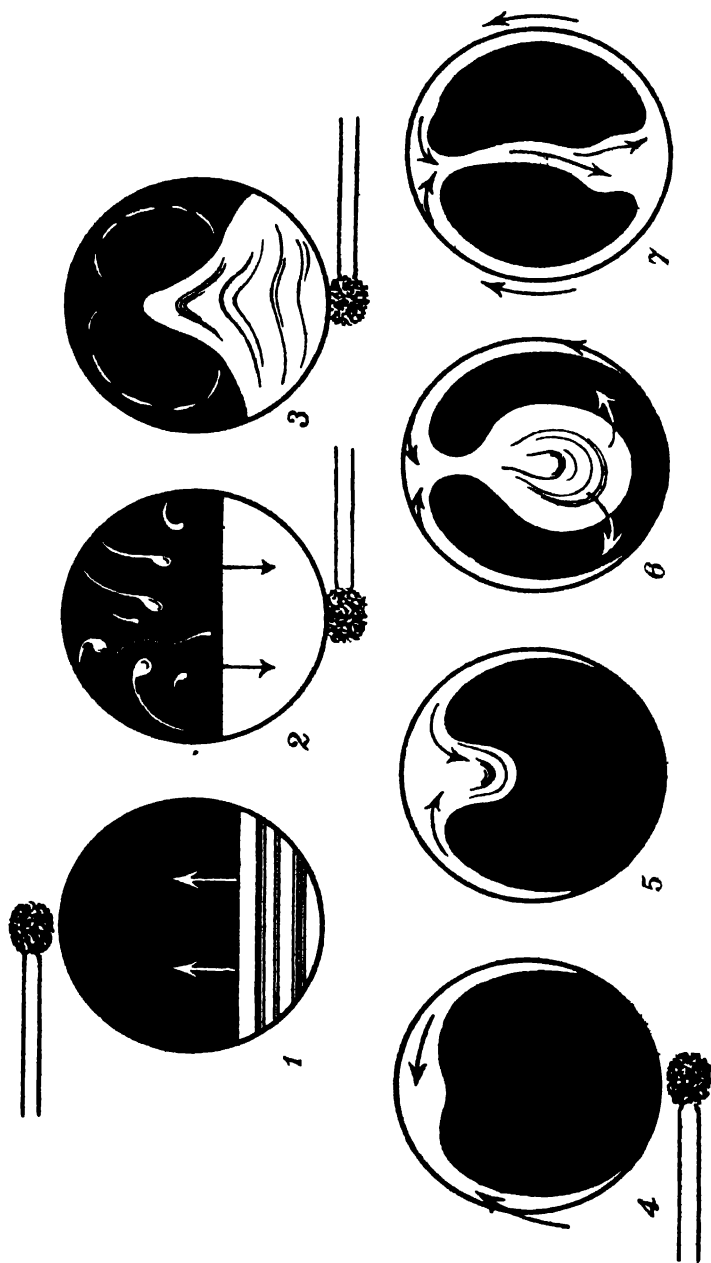


FIG. 9

course, the whole film can be obtained in a condition too thick to show colouring. Such a film, however, when once more left quiet, thins out again at a much greater rate than a newly thrown film, which of course has an excess of undrained liquid on the glass surfaces in the neighbourhood of the Gibb layer. In fact it has been found that a film some 3 or 4 cm. diam. thins with extraordinary slowness if formed, e.g., on a cylindrical ring of fine gauze wrapped outside with bibulous paper or worsted wetted with the soap solution. In such a case only feeble colouring is seen even after some hours, showing how thick the film has remained.

To illustrate the stability of the film the portable box form was placed in an ordinary laboratory shaking machine oscillating at about three or four times a second, and the film remained intact for hours. If the movement was in the plane of the film, it became thickened as described above; but if in the perpendicular plane, very little alteration was produced in the distribution of thickness of the bands.

The results produced by difference of temperature in the Gibb ring are well seen in the double bulb. Here again an interchange of liquid between film and Gibb ring takes place. A black or partly black film shows the effects in the most striking manner. If a pad of wool soaked in water about 30°C . to 40°C . is held on the top of a black film (see 1, Fig. 9), in a few seconds a reflecting streak appears at the bottom, and steadily extends up to a broad segment which would cover the whole film surface in a short time. Now place the warm pad at the bottom of the half black film. At once there begins a movement in the surrounding Gibb ring: increasing streams moving up show coloured streaks mounting the arch of the film, breaking out as brilliantly coloured starlike discs, often leaving a streak curving after them through the black, like a stream of meteors across a dark sky. Meanwhile the coloured lower segment of the film thins out and passes through the appropriate stages of colour, while being steadily absorbed downwards, as if to feed the upward moving streams in the Gibb ring.

In an unexhausted bulb the convection currents caused by this treatment give rise to quite different appearances. For example, starting with a film about two-thirds black, while the lower third is banded with colour, and applying the warm pad below, a current of warm air then streams up across the film displacing the liquid against the gravitational and surface tensional forces which tend to maintain it in its initial condition. A coloured peak is steadily elevated into the dark upper region, and a thin stream of coloured particles begins to rise from the part so elevated, and fall again round the periphery on to the disturbed coloured part below. The original parallel bands have now the appearance of strata bent into finely curved patterns; a very brilliant appearance occurring from the contrast of the silvery and steel-blue portions of the film,

the effect being very much like that of some Japanese lacquer, the simulation of a volcano enhancing this suggestion (see 3, Fig. 9).

In an horizontal film many similar movements may be produced ; the various stages observed in one case are figured at 4 to 7, Fig. 9, the convection finally established passing in a coloured stream across the black film, and back round either side through the Gibb ring.

Variation in the amount of liquid near the Gibb ring has been referred to as being a disadvantage for certain purposes. With the object of avoiding this a ring support was arranged for the film. Platinum wire about 0.2 mm. thick was used, and was sealed in at the neck of the double bulb. The film was thrown as usual ; the peripheral part between the wire ring and the glass was then destroyed either by touching with a glowing pencil of carbon, or more conveniently with a small sponge saturated with liquid air. With such

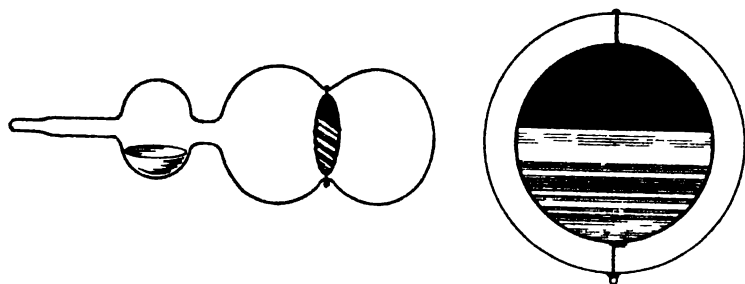


FIG. 10.

an arrangement there is no actual necessity for an open way on both sides of the film to equalise the pressure, because the film hangs free of the glass. A simpler form of double bulb can then be used, with the result that there is greater freedom in illuminating and viewing the film. This was found to be especially desirable with the use of ultra-violet light, for which purpose a quartz bulb was obtained of the shape shown in Fig. 10. For some purposes the convex front of the bulb may be replaced by a plane window set at a small angle to the film in order to avoid subsidiary reflections. This form of support is well adapted for showing the permanence of the film under vibration, the wire ring being then sealed to the bulb neck at one point only, and thus behaves as a sensitive index to any vibration communicated to the bulb. A spot of light reflected from the film shows the movement. It can be seen that the film is not destroyed even though strongly vibrating when the ring is projected in profile ;

the amount of the amplitude of the vibrations is seen to exceed 2 cm., in a ring of 3 cm. diameter.

In another form of exhausted vessel, shown in Fig. 11, the film is obtained on a rectangular glass frame. This frame was made of glass rod 0.2 mm. diam., and must be symmetrically placed in the tube. To obtain the film the liquid has simply to be smoothly decanted out of the bulb to the opposite end and carefully returned, taking care that the frame emerges at right angles to the surface of the retreating liquid. The shape of the bulb permits the film to be

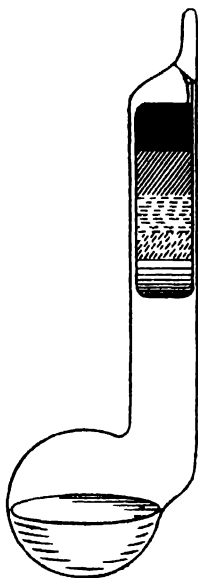


FIG. 11.

set up for examination with either its long or short side vertical, while retaining the liquid in the bulb.

For the measurement of the rate of extension of the black the wire ring or some similar supporting frame is very convenient, as the film is thus completely contained and isolated from excess liquid. The line of demarcation between the black and the remainder of the film is very clearly marked, and with the proper illumination the fall can easily be followed on a cathetometer. Different soap solutions give different results, and temperature effects are very marked. The next table includes some typical results obtained at ordinary temperature with solutions of potassium and sodium oleates approximating in composition to that given by Plateau.

RATE OF EXTENSION OF BLACK ACROSS FILMS OF SOAP SOLUTION.

Exhausted Vessels.

Film 3 cm. diameter, in vertical plane.					mm per minute.
On glass neck	0.20 to 0.05
On wire ring	0.33 to 0.16
On glass frame, 6 cm. \times 1 cm.					
Long side vertical	4.0 to 0.4
Short side vertical	0.2 to 0.016
Film 3 cm. diameter, in horizontal plane					0.09

Unexhausted Vessels.

Films in vertical plane, across glass bottle.					
19 cm. diameter	0.24 to 0.16
3 " "	0.06 to 0.02
Film in horizontal plane, across glass bottle					
3 cm. diameter	0.12 to 0.16

Alteration of Inclination of Plane of Film.

Film on rectangular frame in exhausted vessel.					
Inclined 10 to horizontal	0.04 to 0.01 after 7 hours.
" 20° "	0.15
" 40° "	0.305

In an horizontal film the black circle increased in diameter from 8 to 32 mm. in about 4 hours, the actual rate being 0.11 mm. per minute. It follows that the gravitational effect is considerable.

A 3 cm. film of 2 per cent potass oleate in 50 per cent glycerin, after being freshly thrown, gave a rate of 0.05 mm. in a vertical plane. After the same film had become completely black and drained, it was re-thickened from the remaining Gibb ring by rotation. The rate then measured was 0.2 mm. through the upper third, 0.5 mm. in the equatorial part, and 0.3 in the lower one-third. This was again repeated, when the corresponding figures were 1.6, 5.0 and 1.6. It would thus appear that when the Gibb ring is forcibly deprived of liquid it exerts a very powerful attraction to any liquid in the neighbouring film, quickly draining it to the black condition when the neighbouring surfaces are well drained.

Generally speaking, solutions of potassium soaps thin rather more slowly than sodium soaps of the same composition, and both are much slower than comparable concentrations of ammonium soaps. These last are very sensitive to small variations of ammonia from neutrality, becoming slow when the ammonia is in defect, and vice versa. As regards the percentage of glycerin, as would be expected, increasing concentration reduces the mobility and rate of development of the black, which rate, however, is then more sensitive to changes of temperature than are those solutions having less glycerin. A plane vertical circular film 19 cm. diameter, containing 5 to 10 per cent excess of ammonia over neutral oleate in 50 per cent glycerin, gave

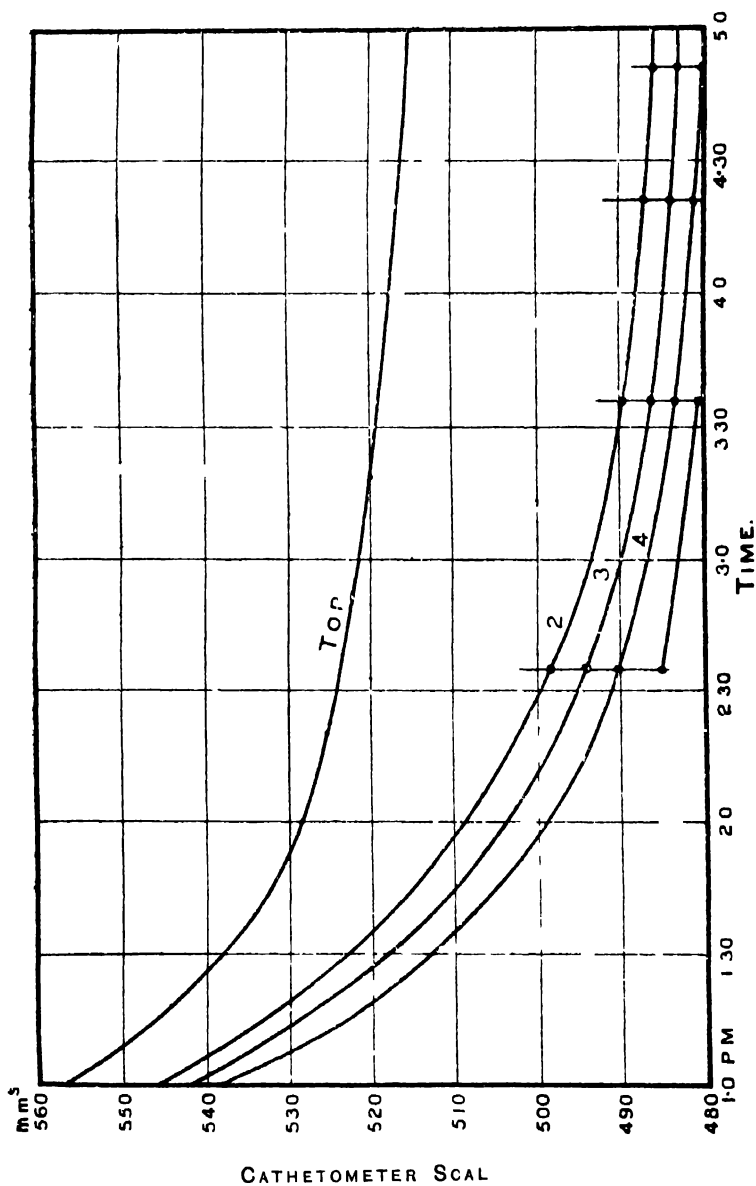


FIG. 12.

a rate of $1\frac{1}{2}$ cm. per hour for vertical fall of black boundary. The black does not generally extend at a steady rate across a circular film. Thus a film on a thin platinum wire ring 3 cm. in diameter, using $1\frac{1}{2}$ per cent potass oleate in 25 per cent glycerin, gave in successive half-hours rates of 0.3, 0.23, 0.18 mm. per minute. This slowing down is to be expected as the black approaches the lowest part, where the ordinary drainage from the film accumulates to form a permanent drop. It follows that a more uniform rate is obtained in a large film than in a small one. Thus in a film on a rectangular frame 8 cm. long vertically by 2 cm. across, a uniform rate of 0.45 mm. per minute was registered through 5 cm.

This last measure was obtained by a solution of $3\frac{1}{3}$ per cent potass oleate in 33 per cent glycerin in the evacuated tube of the form shown in Fig. 11.

In this apparatus the film can be produced under such undisturbed conditions that several grades of black frequently appear between the ordinary deep velvety black and the silvery film which usually directly follows it in order of thickness. As many as five distinct grades have been seen, each perfectly defined in regular proportion by a sharp horizontal boundary line. In the development of the film these extend downwards at different rates, as shown in the accompanying graphs (Figs. 12, 13, 14.)

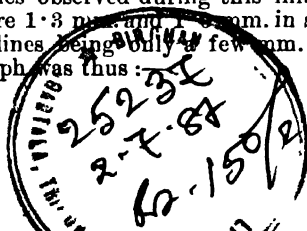
The values of the observed rates in mm. per min. for a 5 per cent ammonium oleate solution in 50 per cent glycerin, in successive periods of 20 min., were :—

					Finally
Top black	0.6	0.5	0.3	0.18	0.06 mm. per min.
2nd "	0.8	0.55	0.45	0.35	0.05 "
3rd "	0.9	0.60	0.48	0.34	0.05 "
4th "	0.95	0.65	0.425	0.33	0.05 "

Comparable observations with a $3\frac{1}{3}$ per cent potass oleate in 33 per cent glycerin gave the following values. Here five grades were detected :—

Top.	Uniform rate of 0.45 mm. per min.			
2nd	0.55	0.375	0.26	"
3rd	0.55	0.38	0.40	"
4th	0.50	0.375	0.26	"
5th	0.40	0.28	0.20	"

Preceding these observations, the 4th and 5th grades had not very definitely separated. The values observed during this initial period for the 2nd and 3rd grades were 1.3 mm. and 1.5 mm. in succeeding 10 min.; the two separating lines being only a few mm. apart and parallel. The form of the graph was thus :



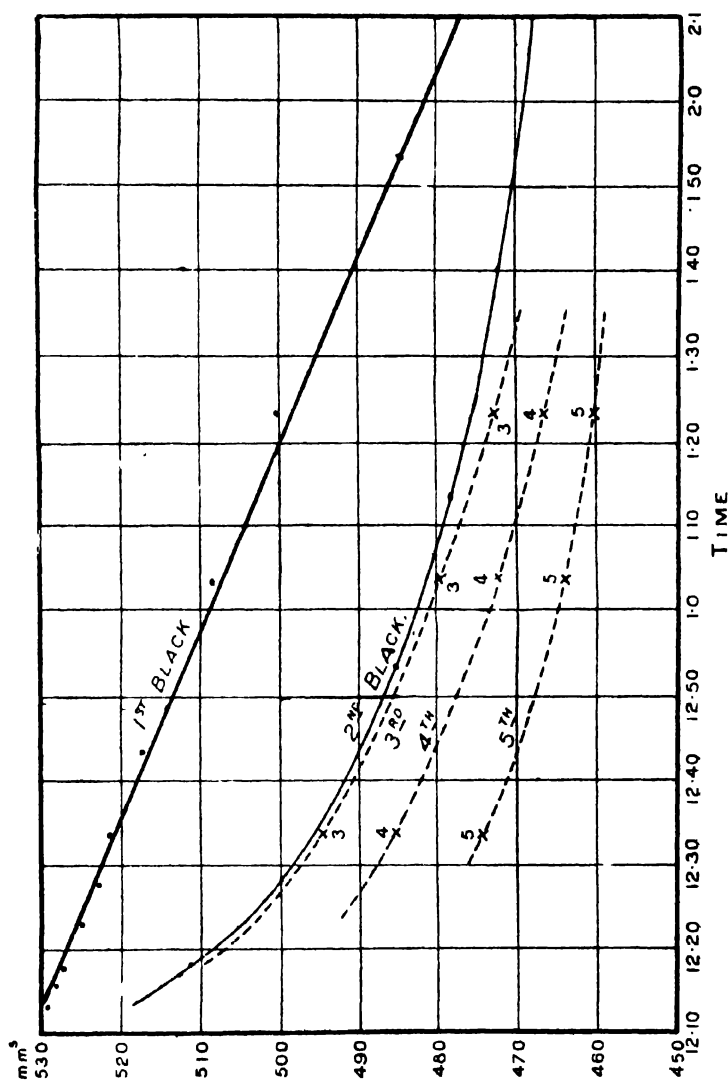


FIG. 13.

Instead of taking the measures with the film vertical, observations were made at an inclination of 40° to the horizontal, with the following result :—

Inclined 40° .	0.305 mm.	1st black
"	0.65	" 2nd and 3rd blacks
"	0.90	" 4th black

For a more extended study longer films must be used. These graded blacks appear to be rather unstable. At times they become grained and indefinite under slight stimulus of vibration or change of temperature. A very striking effect is produced by cautiously flowing a little solution through the lower part of the graded film; the various grades then become mottled, and coalesce with rapid aggregation to the stable silvery boundary. This effect sometimes occurs apparently spontaneously. With solutions of ammonium oleate, slight excess of tension of ammonia seems to be a predisposing cause, easily brought about by a small elevation of temperature.

The form of graph observed in such a case is next shown. The film started with development of three grades of black, which suddenly coalesced to the common single stage, which then extended at a fairly uniform rate.

Rate before coalescence	... 1st	0.40 mm. per min.
" "	... 2nd	1.50 "
" "	... 3rd	1.45 "
Rate after coalescence	steady at	0.8 "

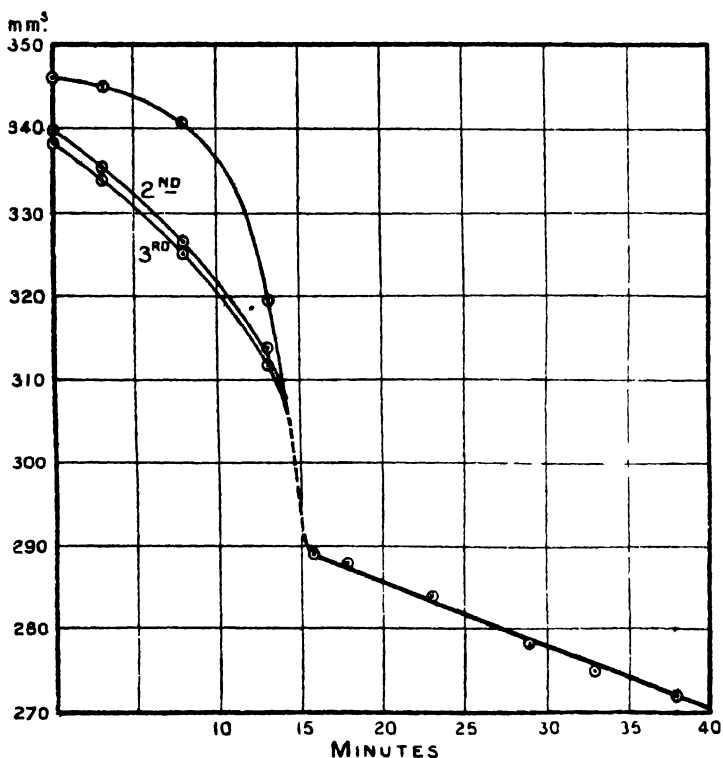


FIG. 14.

COLOUR VARIATIONS.

The colours shown by liquid films are the index of their thickness, becoming especially definite as the greatest tenuity is reached. The limit in this direction is the so-called black film, by which is meant a film too thin to cause colour by interference.

A liquid film has two reflecting surfaces, so that the light coming from the film is due to reflection from the upper and the lower surface. This latter portion will have travelled a slightly longer path than the first, and in a denser medium, where its velocity is lower. The vibrations will thus emerge out of step or beat with the part reflected at the upper surface, which has travelled only in air, and interference between the two portions must follow. This will depend in amount on the length of the path in the liquid, that is, on the thickness of the liquid film and the inclination of the path of the light to the reflecting surfaces. When the film becomes very thin, the length of this path in the liquid approaches the order of a few wave lengths of light, and the interference effect will then become appreciable. If the light be monochromatic, that is, composed of one wave length only, alternate light and dark bands will be seen varying in character with the specific monochromatic light. When composite light is used, as in the case of ordinary white light, various wave lengths will be successively suppressed as the thickness of the film decreases, and the reflected light being deprived of these will accordingly appear coloured.

The limiting case of the "black" film is obtained when the thickness of the film is very small compared to the wave length of ordinary light; no sensible interference can then be caused in the film because of the extreme shortness of the path therein. However, all the rays that have been reflected *in* the liquid—i.e., from the lower surface—suffer no modification; those which are reflected *on* the liquid are retarded or held back half a beat, and will thus be completely out of step with those coming out from the lower surface, with the result that an apparent blackness results. Such feeble light as there is appears neutral and faint on a dark ground, and represents, so to speak, no more than the difference in general intensity suffered by the internally reflected light, due to the slight absorption in the film.

In the same way the light passing through the film becomes coloured. The two portions now producing colour by interference may be regarded, on the one hand, as that which has simply been bent or refracted slightly in passing through the film; and, on the other hand, as that which instead of passing straight through is reflected up from the lower surface and down again from the upper surface before following the course of the unreflected beam. The amount of retardation in the film is the same as was the case between the two reflected portions of light previously considered. But none

of the transmitted light is reflected on the liquid, and therefore it does not suffer the phase change of half a beat already referred to. The resulting colours will therefore be complementary to those produced at the same time in the reflected light, because the amount of interference will be uniformly different by this half beat, the vibrations suppressed in the reflected illumination being present in that transmitted, and vice versa. The limiting case of the very thin film appears bright by the transmitted light, since no appreciable retardation occurs in the passage through the film; and the phase change of a half beat giving the black film by suppression of the reflected light does not happen in the transmitted light.

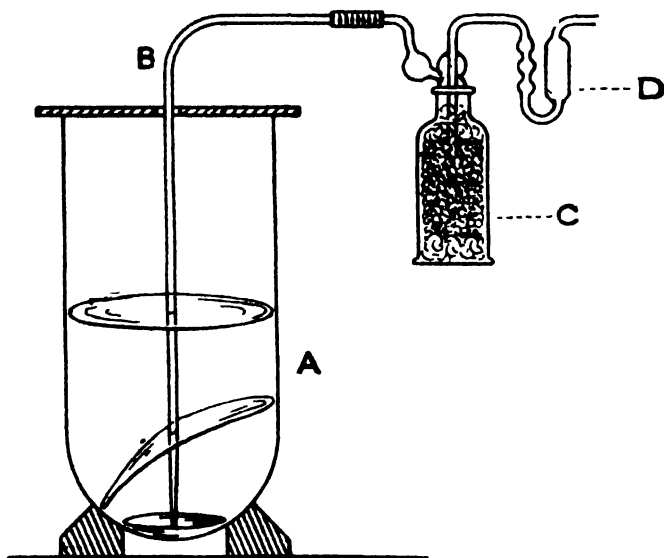


FIG 15.

A simple method of obtaining a soap film of about 25 cm. diam. is illustrated in Fig. 15. An inverted cylindrical glass shade A containing slight depths of soap solution has its inside surface thoroughly moistened by careful tilting and rotating. A glass cover pierced with a hole large enough for a convenient length of quill tube B to pass was bent at right angles and connected to the outlet of a gas washing bottle C charged with granular soda lime to purify the air from carbonic gas and cotton wool to remove all suspended matter. A bubbler U-tube D attached to the inlet of C serves as a convenient mouthpiece and condenses the major part of the water

vapour from the breath, but when large volumes of air have to be used it must come from a gas holder or water pump or compressed air cylinder. After the impurities of the vessel have been removed, dipping B into the solution in A, a small bubble can be blown on the liquid, and this can be expanded until it passes up the wet sides of the cylinder as a flat circular film. The film becomes thin enough to show brilliant rings of colour in less than a minute, these being made brightly visible by holding an illuminated white sheet of cardboard behind and just above the film, while also arranging a black background below the white card. The plane of the film is at right angles to the cylindrical sides, and will thus be level when the cylinder is vertical. In this condition the centre of the film becomes thin enough in a few minutes to show a black circle which steadily extends in diameter until, after some hours, the whole film is black. Such black films under these circumstances may be kept for a year.

Around the black circle as first seen there is a ring of silvery white very sharply marked off from the black. The silvery region then grades very smoothly into pale and deep golden, becoming orange and deep amber, then a brownish madder and full purple, clearing into a bright steel blue. This grades into greenish blue and fades into a light gamboge, developing into a more greenish yellow, and then to a brilliant green. After becoming again yellow, a crimson tint develops and intensifies to a full purple, followed by an extremely intense grass green. This ends the most striking part of the colouring, the increasing thickness being then denoted by alternate red purple or pink and green bands of diminishing depth of colour until they fade into the transparent colourless thick film.

These flat films have a position of equilibrium relative to the supporting vessel, tending to set at right angles to the plane of the walls at the place of contact; thus the film in the cylindrical glass shade remains flat, because that is the plane perpendicular to the supporting walls. If a film be similarly blown across the centre of a spherical flask, then at any inclination this condition will be fulfilled, and a uniform film should be able to remain in any position if it has the full diameter of the sphere. When there is the minimum of liquid and the film is well drained, and consequently nearly uniform in thickness, it is seen to remain practically quiet in all positions. When, however, a few c.c. of soap solution are left in the flask, the film is much thicker in the lower part, and, if, further, it is well moistened where it comes in contact with the flask, is more mobile and tends to assume a vertical plane, because the thicker part will sink to the lowest position, whence it will quickly revert when tilted. The appearance when projected on the screen shows that, however the flask be rotated, the film remains very nearly vertical. It will, however, remain fairly steady in any position if it is slightly less than the full diameter of the spherical flask, and is blown up clear of the excess of liquid. When this modification is employed a striking

demonstration of the colour effects can be made by using the film as a mirror for an intense parallel beam of light condensed from an arc lamp. The reflected light is focused by a simple lens combination, and after reflection at a plane mirror can be seen in full detail on the screen. For this purpose a film is blown across the centre of a flask about 5 in. in diameter. The Epidiascope affords a convenient means for the illumination and projection. The film is kept inclined at about 10° or 15° to the horizontal; in a short time the black shows as a segment of the circular film, steadily increasing in extent from the top. The sharply defined line separating this black segment from the rest of the film makes it appear as if cut off. The continual movements in the film can be clearly seen. These are extremely complex, and consist largely of streams of liquids of varying thickness. Therefore they appear in a beautiful variegation of colours well contrasted from the general tone of the region of the film across which they move.

Every local disturbance of the delicate equilibrium is shown by coloured streams or wandering coloured areas of various sizes, usually tending to a circular shape. These, however, by collision or mutual attraction, while moving at different speeds in neighbouring paths, are frequently drawn out into threads and chains which cross the path of another moving circle, and are thus, or otherwise, broken, when a separation takes place into a line of small particles in the manner of the beads on a spider-web. These motions are most strikingly seen when they cross the black area of a film; a condition which is readily produced by small local differences of temperature in the Gibbs ring. Then a stream of coloured starlike discs breaks out from the Gibbs layer, and pass like rockets through the black region, giving a brilliant variety of effects as their many-coloured trails cut and coalesce,

Mr. W. J. Green, B.Sc., of the Davy Faraday Laboratory, has rendered valuable aid in the Research, and Mr. J. W. Heath, F.C.S., of the Royal Institution, has also assisted in the experiments.

Friday, March 24, 1916.

SIR JAMES REID, BART., G.C.V.O. K.C.B. M.D. LL.D. F.R.C.P.,
Vice-President, in the Chair.

PROFESSOR W. M. BAYLISS, M.A. D.Sc. F.R.S.

The Mechanism of Chemical Change in Living Organisms.

IF we take a general view over the large field of chemical reactions known, we notice that there is a great variety in the *rate* at which these reactions take place. Some, and especially those in which electrical forces play a part, reactions between inorganic ions, are practically instantaneous. They are familiar to all in the precipitations of the analytical chemist. Others, such as the hydrolysis of cane-sugar by water, are so slow as to be incapable of detection at ordinary temperatures, unless a very long time is allowed. There are, moreover, all possible stages intermediate between these extremes. Reactions between carbon compounds are, generally speaking, comparatively slow; but, as the name "organic" indicates, they are the characteristic changes of the living cell.

Early workers in the domain of physiological chemistry—Schönbein, for example—were struck by the fact that reactions which require, in the laboratory, powerful reagents, such as strong acids and high temperatures, to make them take place at a reasonable rate, occur rapidly in the living organism at moderate temperatures and in the presence of extremely weak acids or alkalis. I may refer to the decomposition of proteins into their constituent amino-acids, which is a part of the normal process of digestion, but, when ordinary laboratory methods are used, requires boiling for several hours with concentrated hydrochloric or sulphuric acid.

The problem before us, then, is to discover how a slow reaction can be made to go faster. The most obvious and well-known method of doing this is by raising the temperature; but this is clearly out of the question in living cells. Another possibility is to make use of mass action, increasing by some means the effective concentration of the reacting substances; in this way the number of contacts per unit time would be raised. This is possible in the cell. There remains a third, the formation of an intermediate compound with another substance. This compound may be supposed to be both formed and again decomposed at a rapid rate, so that the total time taken is much less than that of the original reaction.

Now it is evident that something of the kind contemplated by these two latter possibilities is at the bottom of the process called "catalysis" by Berzelius. This chemist directed attention to the numerous cases known, even at his time, where the presence of a third substance brings about an enormous acceleration of a reaction, without itself taking part in it, so far as appears at first sight; at all events, this third substance reappears at the end unchanged. An example is the effect of finely divided platinum on hydrogen peroxide. Similar phenomena were known to Faraday, and described by him about the same time, but without giving them a special name.

Agents of this kind were soon discovered to be present in living cells. Such catalysts are called, for convenience, "enzymes," as suggested by Kühne, although there is no real scientific necessity for the name. That of "ferments" is still sometimes used, and is not now liable, as it was in Kühne's time, to cause confusion by application to living microbes.

Since catalysts are, as a rule, found unchanged at the end of their work, it is clear that they do not themselves afford energy for the purpose. Indeed, the energy change of a catalysed homogeneous system is the same as that of the reaction when proceeding at its ordinary slow rate. How, then, do they act?

The first thing to note with respect to enzymes is that they are capable of activity in media in which they are insoluble. Whatever may be the nature of this activity, therefore, it is exerted by the surface of the catalyst. We may then reasonably ask, as the most obvious hypothesis, is there ground for holding that the increased rate of reactions brought about by enzymes is effected by increase of concentration of the reagents at the surface and consequent acceleration of the reaction by mass action? We know that substances which lower surface energy of any form are concentrated at such boundary surfaces. The process is well known as "adsorption," and is a consequence of the operation of the principle of Carnot and Clausius, which states that decrease of free energy always occurs, if it is possible for it to do so. In fact, such an explanation was given by Faraday of the effect of metallic platinum in causing combination of oxygen and hydrogen gases. Although the name "adsorption" was not used in this description, Faraday had very clear ideas of the process, and gives several interesting cases. He showed that the necessary condition for the activity of platinum in the case referred to is a chemically clean surface, in order that the gases may condense on it. It matters not whether the removal of deposit is effected by mechanical polishing; by the action of acid or of alkali; by oxidation or reduction—making it either anode or kathode in an electrolytic cell will serve. It should be mentioned that this view did not receive universal acceptance, but the fact that it recommended itself to the keen insight of Faraday is powerful evidence in its favour.

I would not venture to state that this hypothesis is yet in a

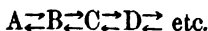
position to explain all the facts met with in the action of enzymes themselves, but it is remarkable how many receive a satisfactory account. We are at once confronted by the difficulty of the considerable number of different enzymes. But we must not forget that adsorption is controlled by a great number of factors in addition to mechanical surface tension. All those properties which suffer modification at phase boundaries play their part—electrical charge, solubility, compressibility, even chemical reaction itself, may be mentioned. Moreover, as Hardy has pointed out, the act of condensation in itself may well be accompanied by the manifestation of molecular forces which result in increased chemical potential of the reacting substances. It is clear that experimental decision of the questions involved is almost impossible until we have in our hands pure preparations of enzymes. We cannot as yet exclude the possibility of the formation of intermediate *chemical* compounds between enzyme and substrate, but their existence has not been demonstrated, and what I may venture to call Faraday's view has the advantage of simplicity, and thus the support of William of Occam's "razor."

The important question of the synthetic action of enzymes demands a little attention at this point. All reactions may be regarded as being, in principle, reversible or balanced, and the greater part of those of the living organism are found experimentally to be so. If we take for consideration those enzymes the action of which consists in the addition or removal of the elements of water, we find that, as would be expected from the law of mass action, the position of equilibrium in the presence of a large excess of water is very near to that of complete hydrolysis, and this is the state of affairs in the usual laboratory experiments. On the other hand, the less water is present, the greater is the preponderance of the opposite—synthetic—aspect. Take the classical case of ethyl acetate. If the ester and water are mixed in molecular proportions, hydrolysis to acid and alcohol occurs until two-thirds of the ester are decomposed. Moreover, the same final composition is obtained if we commence with acid and alcohol, and so work in the other direction. But these reactions proceed by themselves with extreme slowness, taking months before coming to an end. But the presence of a catalyst, such as mineral acid, brings about equilibrium in an hour or so, and we notice that it is the same as the spontaneous one. An enzyme, known as lipase, also brings about equilibrium rapidly. The important point in respect of the mechanism of living cells is that by changing the available amount of water, the reaction may be made to proceed in either direction at will. The series of curves given by Armstrong and Gosney (Proc. Roy. Soc., 88B, p. 176) show this fact very clearly. Further, if the equilibrium is brought about rapidly, even if to any position except that of complete change in one or the other direction, the enzyme must accelerate *both* reactions, and any hypothesis of special "synthesising" enzymes is superfluous. This is essentially

the position taken by van't Hoff in the work with which he was engaged at the time of his death. What is required, then, is a means by which the cell is enabled to change the available water at the disposal of reactions occurring therein. We do not as yet know the precise nature of such mechanisms, but there is reason to believe that they are provided by changes in the surface area of colloidal constituents or in the power of imbibition possessed by certain contents of the cell.

We here come across an interesting problem which cannot be said to be solved satisfactorily at present. We have seen that the equilibrium position of an ester system when reached rapidly under the action of a soluble catalyst is the same as the spontaneous one. But there is a certain difference when a heterogeneous catalyst, or enzyme, is used. Nevertheless, the equilibrium is a true one, being in the same position when approached from either end. The amount of butyric acid combined as amyl ester in a particular system under acid catalysis was found by Dietz to be 88 per cent. of the total; under the action of the enzyme lipase it was only 75 per cent. This fact has given rise to various suggestions, and has troubled people's minds because it appears to give a possibility of evading the second law of energetics. Now, it was pointed out to me by Prof. Hopkins that, on the hypothesis of a rapid attainment of equilibrium by condensation on the surface of the enzyme, it is necessary, if the natural equilibrium is to be unaltered, that adsorption of all the components of the system should be the same proportion of each, because the position of equilibrium must be the same on the surface of the enzyme as that which results in the body of the solution. In the presence of a large excess of water, it does not seem likely that a difference of equilibrium owing to this cause could be detected. But this should be possible when the equilibrium position is nearer the middle, so to speak, and I am at present engaged in experiments on the question. At any rate, difference in adsorption may be the cause of the phenomenon of Dietz. It would simply imply that water is adsorbed by the enzyme in relatively larger proportion than the other constituents of the system. It should be remembered that the solvent in these experiments was amyl alcohol containing about 8 per cent. of water, and, as Arrhenius has shown, all substances present are adsorbed, although the laws governing the relative proportion of these various substances are not yet completely worked out.

We see, by consideration of the facts relating to the action of enzymes, how important a part is played by changes in the rate of reactions, and there are two further points to which attention has been directed by Prof. Hopkins. Take, first, a series of reversible reactions in which the products of one form the starting-point of the next following :—



If the rate at which B is converted into C is greater than that at which A changes into B, it is obvious that the amount of B present at any moment may be extremely small, although the whole of the final products have passed through the stage. The fact warns us from estimating the importance of any particular constituent of the cell by the quantity to be obtained.

The second point is this. Suppose that there are two independent reversible reactions, both leading to the same product, C,



and that $A \rightarrow C$ is more rapid or easier than $B \rightarrow C$. This latter reaction will be practically absent, being balanced by the excess of C. But, if the former reaction is abolished by the removal of A, then $B \rightarrow C$ will take place in proportion as C is used up in other reactions. Thus, under special conditions, a reaction may take place which is not detectable under normal conditions, although capable of taking place.

One of the most difficult questions is the manner in which the various components of the cell are prevented from entering into chemical reaction except when required. Enzymes, for example, are not always in activity. The conception which states that the cell consists of numerous minute "reaction chambers," separated from one another by membranes, seems to present most possibilities. These membranes must be regarded as capable of removal and of reconstruction, or reversible as regards their permeability. The food vacuoles of an Amoeba may serve as an illustration of such chambers on a comparatively large scale. In these vacuoles digestion processes are going on independently of other reactions in various parts of the same cell protoplasm, although this latter behaves as a liquid.

The general conclusion to which we arrive is that velocity of reaction plays an exceedingly important part in the regulation of cell mechanics. I venture to think that the conception is destined to replace static points of view, such as that of "lock and key" or the fitting together of molecular groupings. That there is still very much to be discovered is obvious. We have to find out how the living cell is able to modify and adjust together the large number of reactions known to the chemist. The study of the methods by which the rate of these reactions is affected is one of the most valuable of those accessible to us.

[W. M. B.]

Friday, March 31, 1916.

EDWARD POLLOCK, F.R.C.S., Vice-President, in the Chair.

PROFESSOR A. FOWLER, F.R.S., Sec. R.A.S.

The Spectra of Hydrogen and Helium.

THE investigation of the spectra of hydrogen and helium is intimately connected with problems apparently so diverse as the constitution of the atom and the order of celestial evolution. Hydrogen is remarkable as yielding the simplest of all known spectra, and, though helium ordinarily presents greater complexity, it is now believed to be capable of emitting another spectrum which rivals in simplicity that of hydrogen itself. These simple spectra naturally make a special appeal to those who are attempting to calculate the spectra of the elements from theoretical considerations relating to the structure of atoms, for here the problem is reduced to its simplest terms. The two elements are also of exceptional interest to astronomers, for hydrogen shows itself in nearly every self-luminous celestial body which has been observed, while helium is characteristic of an important special class of stars. Indeed, helium, as everyone knows, received its name from the occurrence of its yellow line D_3 in the sun's chromosphere, long before it was discovered on earth by Ramsay; and the spectrum of hydrogen is more completely displayed in some of the stars, and in the chromosphere, than in any laboratory experiment which has yet been made. It may therefore be of interest to bring together some of the principal results which have been obtained in connexion with the spectra of these two elements.

Let me first recall the spectrum of hydrogen, which we can readily obtain from a hydrogen vacuum tube. If we take a tube at random we shall most likely see two spectra superposed. One of them consists of many hundreds of faint lines, constituting what is called the *secondary spectrum*, while the other includes the well-known lines of the so-called *primary spectrum*, beginning with H_α in the red, and following on with H_β in the blue-green, H_γ in the blue, and so on. Either of these spectra can be suppressed, or nearly so, at will. Generally speaking, narrow tubes or strong discharges favour the primary spectrum, while the secondary is best developed in wider tubes or with weaker discharges.

Although for some time considered as possibly due to impurities,

it is now generally conceded that this secondary spectrum really belongs to hydrogen. The spectrum is so complex as almost to defy analysis, but an important beginning has been made by Fulcher, who has shown that some of the constituent lines in the green and red are arranged like those of a band spectrum. These particular lines are relatively stronger at low pressures, and their near equality of step is clearly seen in small-scale photographs. On current theories, these band lines would be considered to emanate from hydrogen molecules, but it is not yet certain that this is true of all the lines of the secondary spectrum, as some of them show considerable Zeeman effects in the magnetic field. The secondary spectrum offers less attraction to astronomers than to physicists, for it has not yet been recognized in any celestial body whatsoever.

The primary spectrum of hydrogen is of more immediate interest. It may be obtained conveniently from an ordinary vacuum tube having a narrow capillary, if the gas be at a pressure of a few millimetres. Sealed tubes, however, soon deteriorate, in the sense that

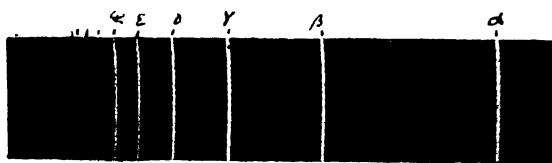


FIG. 1.—Balmer Series of Hydrogen Lines.

they give undue prominence to the secondary spectrum at the expense of the primary. Mr. Guild, of the National Physical Laboratory, has lately shown that this arises from increase of pressure caused by the evolution of gas from the electrodes, and that the life of a tube intended for the primary spectrum may be much prolonged by the addition of a large bulb, so that the rate of increase of pressure is much reduced. You will observe that the red glow of this tube is in striking contrast with the blue of the tube which gave us a strong secondary spectrum.

When we examine the primary spectrum, we are at once struck by the wonderful regularity in the arrangement of the lines (Fig. 1). We see how the lines gradually become closer together and diminish regularly in intensity as we pass from the red to the ultra-violet. It was not until 1885, however, that the law connecting the lines was discovered. It was then found by Balmer that the wave-lengths of the known lines could be accurately expressed by the simple formula

$$\lambda = 3646 \cdot 14 \frac{m^2}{m^2 - 4}$$

where λ is the wave-length in Ångström units (10^{-10} metre), and m takes the value 3 for H_{α} , 4 for H_{β} , and so on.

It is instructive to re-write the equation in the form

$$\lambda = 3646 \cdot 14 + \frac{3646 \cdot 14 \times 4}{m^2 - 4}$$

from which we see at once that there can be no members of this series beyond $\lambda 3646 \cdot 14$, for this is the value of λ when m is infinite. The wave-length $3646 \cdot 14$ is thus the end, or "limit," of the Balmer series.

In such formulæ there are often very definite advantages in expressing the positions of the lines in wave-numbers rather than in wave-lengths, the wave-number being $10^8/\lambda$, or the number of waves per centimetre, corrected to vacuum. In these terms, the Balmer formula becomes

$$n = 27,418 \cdot 75 - \frac{109,675}{m^2}$$

or

$$n = 109,675 \left(\frac{1}{2^2} - \frac{1}{m^2} \right)$$

Balmer's formula clearly permits the calculation of an indefinitely great number of lines, but in laboratory experiments even ten or a dozen are not obtained without a little trouble. Sir James Dewar has found that admixture with helium tends to the better development of the ultra-violet members of the series, but it is in the white stars and in the sun's chromosphere that the Balmer series is most completely exhibited. In some of the stellar spectra photographed by Sir William Huggins we can count up to about the 20th member. In the chromosphere, during eclipses, the Astronomer Royal has photographed as far as the 28th, and Professor Mitchell as far as the 34th line. The Balmer formula continues to represent the lines with astonishing accuracy, so that no one hesitates to attribute the ultra-violet members to hydrogen, although experimental proof of their hydrogen origin is entirely wanting.

Besides the Balmer series there are other lines of the primary spectrum of hydrogen which do not come within the range of ordinary observation. There is an infra-red series which was predicted by Ritz and observed by Paschen; and another series in the extreme ultra-violet which has been partially recorded by Lyman with a Schumann spectrograph. These two series run parallel to the Balmer series and are simply related to it, as we shall see later.

The number 109,675 which occurs in the Balmer formula is an important physical constant, and at the Imperial College Mr. Curtis has taken a great deal of trouble to ascertain its precise value. He obtained a fine series of photographs with the 10-foot concave

grating, and it is believed that an accuracy approaching one-thousandth of an A.U. was attained in the measures. The new value for the "Rydberg constant," when expressed on the International scale, is $109,679.22$, but this is not final, as it was not possible to take account of the fact that H_{α} and H_{β} are very close doublets, which could not be separately measured with the instruments available.

Balmer's discovery of the law connecting the lines of hydrogen soon led to the recognition of numerous somewhat similar series in the spectra of other elements, chiefly through the labours of Kayser and Runge, and of Rydberg. In place of the simple series shown by hydrogen, however, it was found that other spectra usually included several series superposed, so that in many cases the regularity in the arrangement of the lines was only disclosed after patient investigation. Lithium provides one of the simplest examples, and in Fig. 2 we may observe how the seemingly irregular spectrum has been resolved into several series, each of which bears a

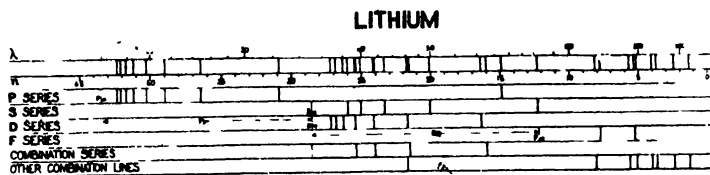


FIG. 2.—Series Lines of Lithium.

general resemblance to the hydrogen series. Usually there are three chief series, designated, in order of brightness, the Principal, Diffuse, and Sharp series. There are also certain subsidiary series, of which the one called the Fundamental series is perhaps the most important.

The Balmer formula is not applicable to any other series without modification, and Rydberg adopted the general formula

$$n = A - \frac{N}{(m + \mu)^2}$$

where A is the limit of the series, N the number $109,675$ derived from hydrogen, and μ usually a fraction. This formula is only approximate, but it was sufficiently exact for the discovery of important relations between different series occurring in the same spectrum. Thus, the limits of the Sharp and Diffuse series are identical, and differ from the limit of the Principal series by an amount equal to the wave-number of the first Principal line. Similarly, the limit of the Fundamental series differs from that of the Diffuse series by an amount equal to the wave-number of the

first line of the Diffuse series (see fig. 2). The chief relations are embodied in the following formulæ given by Rydberg :

$$\text{Principal series : } P(m) = N \left(\frac{1}{(1+s)^2} - \frac{1}{(m+p)^2} \right)$$

$$\text{Sharp series : } S(m) = N \left(\frac{1}{(1+p)^2} - \frac{1}{(m+s)^2} \right)$$

$$\text{Diffuse series : } D(m) = N \left(\frac{1}{(1+p)^2} - \frac{1}{(m+d)^2} \right)$$

where p , s , and d are the values of μ for the respective series. The main point I wish you to observe is that the Principal and Sharp series are so related that if one of them be known the other can be immediately calculated from it by a mere transposition of terms. More accurate formulæ have since been employed, but the formulæ of Rydberg are the simplest and are sufficiently accurate for our present purpose.

Coming now to the spectrum of helium, it was found by Runge and Paschen that the lines could be included in six series : a Principal, Sharp, and Diffuse series of very close doublets (including the yellow line D_3 at $\lambda 5876$), and a similar set of series of single lines. A portion of the spectrum is shown in Fig. 3.

The existence of two complete sets of series, with no recognized connexion between them, was for some time thought to be an indication that helium was a mixture of two gases, and the supposed element giving the family of single-line series was even named "parhelium." This idea was not wholly dependent on spectroscopic observations, but was apparently strengthened by the fact that either of the two systems could be developed with greater intensity than the other by varying the conditions of discharge. Thus, one of the tubes exhibited glows with a pale green light and shows the single line series most strongly, while the other shines with a yellow light and specially emphasises the doublet series. Helium, however, is not unique in showing such variations, or in giving more than one family of series, and the view that it might be a mixture of gases has long been abandoned.

Helium, like hydrogen, has also a very complex secondary spectrum, though it escaped notice for many years. It was missed, I think, because those who made helium-tubes in the early days were too sparing of the gas. It was discovered independently at the Imperial College and by Goldstein, and may be obtained quite brilliantly in the wider parts of a tube containing helium of sufficient density, if a small condenser and spark-gap be included in the circuit. This spectrum is definitely banded, but although each band is built up on the standard pattern for bands, some of them are arranged in accordance with the law of line series. In this respect helium is

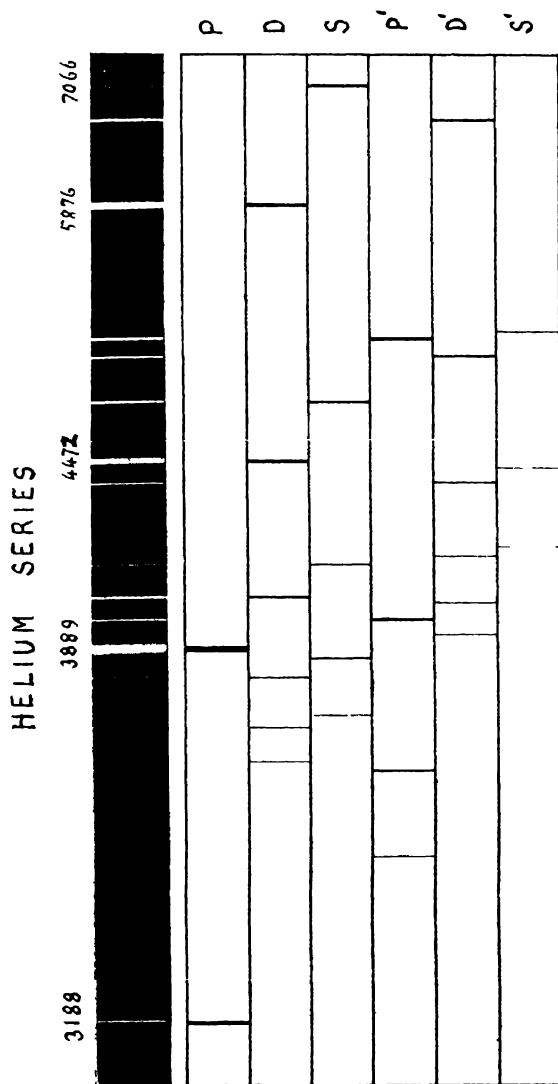


Fig 3 --Spectrum of Helium, showing arrangement in Series.

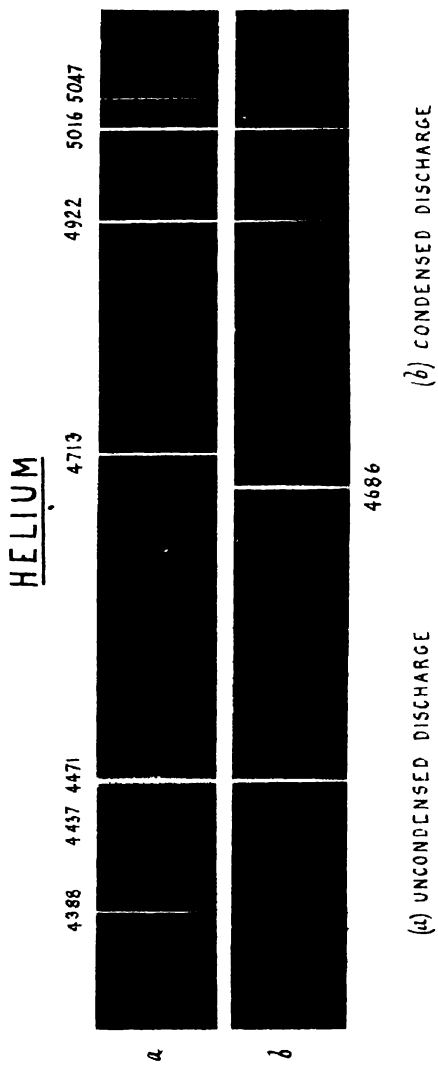


FIG. 5 —Spectrum of Helium Tube, with and without Condenser.

unique. The helium *bands* are not known to occur in any celestial spectrum.

The *line* spectrum of helium, however, is abundantly represented in the heavens. All the principal lines occur as bright lines in the chromosphere, though they do not ordinarily appear among the Fraunhofer lines in the spectrum of sunlight. They are also the characteristic feature of the "helium stars," many of which are found in the constellation of Orion.

A very important chapter in the story of hydrogen and helium was opened in 1896 by Professor Pickering's discovery of a new series of lines in the spectrum of the star ζ Puppis (Fig. 4). These lines occupy positions intermediate between the lines of the Balmer series, and within the limits of error of the measurements, the two series appeared to converge to the same limit. Also, if in the Balmer formula m be given successive values $3\frac{1}{2}$, $4\frac{1}{2}$, &c., the resulting wave-lengths are in close agreement with those of the Pickering lines. Now, these relations are appropriate to two subordinate series

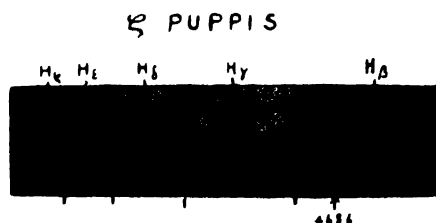


FIG. 4.—Spectrum of ζ Puppis

of the same element, and it was at once suggested by Pickering that the new series might also be due to hydrogen. Rydberg took up the question, and concluded that the Pickering lines formed the Sharp and the Balmer lines the Diffuse series of hydrogen, and he proceeded to calculate the Principal series from the Sharp in the way I have already indicated. Rydberg's scheme for hydrogen, in wave-numbers, thus became

$$n = 109,675 \left\{ \frac{1}{2^2} - \frac{1}{m^2} \right\} \quad (\text{Balmer series})$$

$$n = 109,675 \left\{ \frac{1}{2^2} - \frac{1}{(m + 0.5)^2} \right\} \quad (\text{Pickering series})$$

$$n = 109,675 \left\{ \frac{1}{1.5^2} - \frac{1}{m^2} \right\} \quad \left(\begin{array}{l} \text{Calculated} \\ \text{Principal series} \end{array} \right)$$

giving $P(1) = \lambda 4688$; $P(2) = \lambda 2794$, &c.

That is, if Rydberg were right, some of the stars ought to show a line in the blue, about wave-length 4688, and it should be very bright because it would be the first member of a Principal series. The other lines were not to be expected in the stars because they lie beyond the region for which our atmosphere is transparent. A very prominent line near 4688—actually at 4686—was in fact already well known in some of the special class of Wolf-Rayet stars, where it occurs as a bright line, in company with fainter bright lines of the Pickering series. It occurs also as a bright line in ζ Puppis, and in many of the gaseous nebulae. A very interesting example of its occurrence is in the Ring Nebula in Lyra, where Max Wolf's photographs show it to be restricted to the apparently dark central space, which must accordingly shine with a feeble blue light.

Rydberg's view as to the constitution of the hydrogen spectrum thus appeared to be amply confirmed by astrophysical spectra. It is true that the new lines had not been obtained in the laboratory, but the numerical evidence of their hydrogen origin seemed strong enough to outweigh this objection. There was thus for many years a pretty general belief that the line 4686 and the Pickering lines were due to hydrogen in a particular state which was only realized under the extraordinary conditions which might conceivably prevail in some of the celestial bodies. Sir Norman Lockyer regarded them as representing one of the last stages of chemical simplification brought about by the action of high temperatures in the hotter stars, and he gave the name "proto-hydrogen" to the supposed simplified form of hydrogen which produced them. The alternative name "cosmic hydrogen" was, I believe, due to Miss Clerke.

The next step in the development of the story arose out of observations of total eclipses of the sun. A high-level chromospheric line in the vicinity of 4686 was first recorded in some photographs which I took for Sir Norman Lockyer in West Africa in 1893; but Rydberg's calculations had not then been made, and its special significance was not apparent. This line was still better shown in another series of photographs which I took under Sir Norman Lockyer's direction in India in 1898; its wave-length was then given as $4686\cdot2$, and it was noted that it might be identical with Rydberg's calculated line 4688. It so happened that in order to facilitate the reduction of the eclipse spectra, a number of laboratory comparisons were photographed with the same instrument, and among these were some spectra of helium tubes. Strangely enough, one of these showed a line not previously seen in helium, and it was apparently coincident with the high-level chromospheric line to which I have referred. The wave-length of this line was given by Lockyer and Baxandall a few years later as $4685\cdot97$. The tube which gave the mysterious line appears to have got broken, and it was not known whether the line was due to an unknown impurity, or to some special condition of discharge which had accidentally been dropped upon.

This old observation was kept in remembrance during occasional experiments on helium extending over several years, until at last the line 4686 was recovered very faintly in a tube which I had prepared for a British Association lecture in the summer of 1912. With this beginning, a systematic investigation resulted in due course in showing how the line might be produced at will, and with almost any desired intensity. Generally speaking, the whole secret was to apply condensed discharges of sufficient strength. The denser the gas, the greater the intensity of the discharge required to produce the line, and the brighter and broader the line obtained. If we make the experiment, you will see that the treatment is rather severe; indeed, the tubes very frequently break down under the strain. In Fig. 5 the spectrum given by a heavy condensed discharge in a tube at about 5 mm. pressure is compared with that given by an ordinary uncondensed discharge in the same tube, and it will be seen that the line 4686 appears with great intensity. At lower pressures the line is less bright, but more sharply defined and better suited for accurate measurement; the resulting wave-length was 4685.98 , in close agreement with the corresponding line in the chromosphere, stars, and nebulae. It was also believed to be in sufficient accordance with the wave-length 4687.88 , calculated by Rydberg for the supposed first Principal line of hydrogen.

Identifications resting on a single line are justly looked upon with some suspicion, but in this case confirmation was apparently given by the presence of other lines calculated by Rydberg at 2733, 2385, and 2253. These lines were not in absolute agreement with Rydberg's calculations, but very nearly so, and within the possible range of error of the formulæ.

Having now obtained the long-sought lines, considerable embarrassment was caused by the fact that more lines were obtained than were expected. Besides the Rydberg lines, there was an intermediate set of lines at 3203, 2511, and 2306. However, as these lines could be put in a series having the same limit as the 4686 series, and as hydrogen might be supposed to have still another peculiarity, they were provisionally regarded as forming a *second* Principal series of hydrogen.

The experiments were less successful as regards the reproduction of the Pickering lines, but three of them were obtained with sufficient brightness for approximate measurement; their wave-lengths were 5411, 4541, and 4200. The difficulty with regard to these lines is, I believe, that the conditions which would be expected to brighten them cause them to become so diffuse as to be unrecognizable, for this is certainly what happens in the case of the ultra-violet members of the 4686 series. The stars manage these experiments rather better than we do.

Since hydrogen was always present as an impurity in the helium tubes employed, the new lines were at first attributed to hydrogen, in

accordance with Rydberg's theory. They seemed to have a close numerical relation to the hydrogen series, and no relation whatever to the lines of helium. Moreover, there was evidence that helium aided the development of the ultra-violet lines of hydrogen, and it was reasonable to suppose that it might also facilitate the production of the lines under consideration. Nevertheless, the idea that the new lines were due to hydrogen was not wholly satisfactory, as the occurrence of lines not anticipated by Rydberg broke the analogy with the series of other elements. It therefore seemed desirable to seek for other examples of such series, in order to test the value of the numerical evidence on which the assignment of the new lines to hydrogen was still so largely dependent.

A series of the same character as the 4686 series, consisting of spark-lines of magnesium, had already been discovered, when fresh light was thrown on the subject from another quarter. Not from the stars this time, but from mathematical physics. In July, 1913, Dr. Bohr published the first instalment of his now famous theoretical investigation of the constitution of the atom in relation to spectral emission, and the lines of the 4686 and Pickering series became of great importance in this connexion.

Beginning with the Rutherford model of the atom, and introducing Planck's conception of the quantum of energy, Dr. Bohr quantitatively derived Balmer's formula for the hydrogen spectrum, and in such a form as to exclude the 4686 and Pickering series entirely. On this theory, the atom of hydrogen is supposed to consist of a relatively massive, but very minute, nucleus which is positively charged, and a single electron in orbital motion around it. The electron may revolve in one of certain specified orbits, subject to ordinary dynamical laws, exactly like a planet in motion around the sun, and in these so-called "stationary states" it radiates no light. When under the influence of electric discharge, we are to suppose that the electron is removed from the nucleus, and that on its return it jumps from one stationary state to another; in so jumping it radiates definite amounts of energy which determine the frequency, and therefore the positions, of the spectral lines. At any instant a given atom only contributes to one line of the series, but the summation of the radiations from a large number of atoms accounts for the whole series.

The helium atom is regarded as consisting of a doubly-charged nucleus of four times the mass of the hydrogen atom, and two electrons revolving round it. Moderate discharges are only supposed capable of detaching one of the electrons, and the ordinary spectrum of helium is emitted when this returns to the system; the theory of this spectrum, however, remains incomplete. Under the action of sufficiently strong discharges, both electrons are considered to be removed from the nucleus. The theory is simpler in this case, and Dr. Bohr derived a formula for the series of lines which should be

emitted when only one of the electrons is regained by the nucleus. In a first approximation, the general formula is identical with that for hydrogen, except that the Rydberg constant has four times its ordinary value. This formula gives lines coinciding in position with the Principal series calculated for hydrogen by Rydberg, and also with those of the supposed second Principal series, and unites them in a single series of a new type. Not only this, a subsequent correction of the formula, no longer regarding the mass of the electron as negligible in comparison with that of the nucleus, accounted *exactly* for the slight differences between the positions of the lines 1686, etc., calculated by Rydberg and those in which they had been observed. Thus, according to Bohr's theory, the new helium-tube lines were to be attributed to a simplified form of helium and not of hydrogen. For the sake of distinction, we may conveniently follow Lockyer's notation and refer to the new spectrum as that of "proto-helium." Bohr's results may then be expressed as follows:—

Hydrogen—

$$N = N^1 \left(\frac{1}{p^2} - \frac{1}{m^2} \right) \quad \begin{array}{l} (p = 3 \text{ for infra-red series.} \\ p = 2 \text{ for Balmer series.} \\ p = 1 \text{ for extreme ultra-violet series.} \end{array}$$

Proto-helium—

$$n = N^1 \left(\frac{1}{p^2} - \frac{1}{m^2} \right) \quad \begin{array}{l} (p = 4 \text{ for Pickering series.} \\ p = 3 \text{ for "4686" series.} \end{array}$$

In the first approximation $N^1 = 4 N$, but taking account of the mass of the electron, the theoretical expressions for N and N^1 are

$$N = \frac{2\pi^2 E^2 e^2 M m}{ch^3 (M + m)}$$

$$N^1 = \frac{2\pi^2 (2E)^2 e^2 (4M)m}{ch^3 (4M + m)}$$

where E, M = charge and mass of nucleus of hydrogen atom; e, m = charge and mass of electron; c = velocity of light; and h = Planck's constant. Using the best available determinations of these quantities, the resulting value for N in the formula for hydrogen is as near to 109,675 as can at present be expected. The ratio of N^1 to N can be determined precisely from the formulæ, as the more doubtful quantities cancel; taking $M/m = 1835$, we find $N^1 = 4.001632 N$, in remarkable agreement with the value determined from the actual spectra. Assuming the truth of the theory, the spectroscopic data thus provide a valuable check on the generally adopted value for the mass of the electron.

Experimental support for Bohr's interpretation of the 4686 series

was seemingly given by the subsequent observations of Evans and Stark, who found, as I have since found myself, that the line 4686 can be obtained from helium tubes which show no trace of hydrogen. But it is always difficult to be certain that no hydrogen remains in the tubes; it is apt to hide itself in the glass, or in the electrodes, and to come out when not expected.

Other evidence in favour of Bohr's view, however, was found in a more general investigation of series of enhanced lines—that is, of lines which are intensified in passing from the arc to the spark spectrum. In the first instance, some additional lines of magnesium associated with the well-known spark line 4481 were discovered, and it was found that they could be arranged in a series of the new variety indicated by Bohr in connexion with the 4686 series of the helium tubes. Further experiments revealed many other enhanced lines of magnesium which had previously escaped observation, and it was found that they formed a large family of related series, generally similar to the ordinary series, but differing from them in requiring a “series constant” having four times the value of that derived from hydrogen. The same was found to be true of the enhanced lines of calcium, strontium and barium.

We have therefore now to recognize two distinct classes of series: (1) series of the arc type, having Rydberg's N for the series constant; and (2) series of the spark type, having $4N$ for the series constant. No relation has been found between the arc and spark series occurring in the same spectrum, and they seem to be as distinct as if they belonged to different elements. A logical extension of Bohr's theory leads to the supposition that series of the usual type are produced when only one electron is detached from each atom by the exciting agency, and those of the spark type when *two* electrons have been removed and *one* is regained by the nucleus.

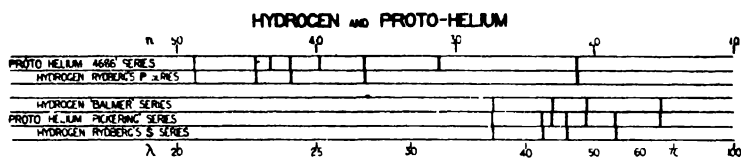
Now the 4686 series is clearly one of the spark type, both as regards its mode of production and the formula which represents the lines. It can therefore no longer be supposed to be associated with the hydrogen series, which is of the arc type. We now see that the numerical relations between them are incomplete, and only approximate, and that they furnish no evidence of a common origin. Taking account also of the experimental results, we are therefore forced to the conclusion that the 4686 series is not due to hydrogen but to helium, as required by Bohr's theory. If it was one theory that led us astray in the first instance, it was another that helped to set us to rights. Nevertheless, the assignment of the 4686 series to a form of helium may now be considered to be independent of any theory.

The chief outstanding point needing confirmation by observation was that the Pickering series—which should run parallel to the 4686 series and also form a series of the spark type—should include intermediate lines very close to the lines of the hydrogen series and on their violet sides, as indicated in Fig. 6. The existence of these

lines could not be proved from the available astronomical data, but at the same time there was no proof of their absence. Experimental evidence on this point, however, has been obtained by Evans, who succeeded after much patient work in photographing some of the lines in the positions predicted by Bohr. Further observations of these lines appear also to have been made very recently by Paschen, but full particulars are not yet to hand. The complete Pickering series, as we now know it, is shown in Fig. 6, from which it will be seen that Rydberg's theory only accounted for one-half of the lines, as was the case with the 4686 series.

Other predictions, relating to the composite structure of the lines of hydrogen and proto-helium, which have been made by Sommerfeld, based upon an extension of Bohr's theory, have also been partially verified by Evans and Paschen independently.

Whatever approach to the truth may be represented by Bohr's theory, it has at least been brilliantly successful in its application to the spectra of hydrogen and proto-helium. Prof. Nicholson has



appear in the spectra of bodies which are generally believed to be at an early stage of evolution. By similar experimental methods, Dr. Merton has, in fact, already shown that some of the most characteristic lines of the Wolf-Rayet stars are probably due to a form of carbon. The surprising thing, to my mind, is that the resources of our laboratories have already proved sufficient for the reproduction of some of the spectral lines which appear to require the most extreme conditions for their development in celestial bodies.

Anyone looking at our extensive maps and catalogues of spectral lines might well form the opinion that we already have quite enough to occupy our attention, but I hope I have conveyed the impression that lines are of varying degrees of interest, and that we may still hope to profit from further attempts to imitate the experiments which are continually in progress in the laboratories of the stars.

[A. F.]

Friday, April 14, 1916.

COLONEL E. H. HILLS, C.M.G., R.E. D.Sc. F.R.S., Secretary
and Vice-President, in the Chair.

PROFESSOR SIR J. J. THOMSON, O.M. LL.D. D.Sc. Pres. R.S. M.R.I.

The Genesis and Absorption of X-Rays.

A YEAR ago I brought before your notice the subject of the production and properties of very soft Röntgen rays. The rays which emerge from an ordinary X-ray tube are produced by cathode rays which have fallen through a potential difference of many thousand volts, while the potential difference for the rays I referred to last year, and to which I wish to recur this evening, varies from 20 to 5,000 volts. I will begin by considering the method of producing the rays and also of the voltage from which they derive their energy. The source of the rays was a tungsten spiral of the kind used in Coobridge tubes, and I am indebted to Mr. Coobridge for his kindness in presenting me with a supply of these spirals. These spirals are heated to incandescence by an electric current, and give out streams of cathode rays, which fall through the voltage between the hot spiral and an anode and acquire energy proportional to the voltage. To get rays of a definite type it is necessary to have means of producing a constant potential difference. One method I have used for doing this is a battery of a large number of small storage cells; another method, which, except for very small voltages, is more convenient and more flexible, is to use a high-tension dynamo designed so that the potential when the speed is constant is not subject to appreciable variation. The one I have used was supplied by Messrs. Evershed and Vignolles, it gives steady voltages from 150 to 5,000 volts, and has proved very satisfactory.

I now pass on to consider the method of studying the character of the Röntgen radiation produced at different voltages. Two methods have been employed: (1) the absorption of the radiation by thin layers of different substances, such as tin, silver, gold, aluminium, celluloid, has been measured; (2) in this method the quantity determined was the velocity of the cathode particles which are emitted by a plate of metal when exposed in a vacuum to the radiation.

When Röntgen rays fall on a plate of metal it emits cathode particles and the speed of these particles, while independent of the kind of metal, increases with the hardness of the rays; indeed there is considerable evidence to show that the energy of the particles is

directly proportional to the frequency of the rays, so that a measurement of this energy specifies in a very convenient way the nature of the Röntgen rays.

The apparatus I used for carrying out the first method is represented in Fig. 1. A is the hot tungsten cathode; G an anode made of gauze; T the target on which the rays strike. These rays pass through the diaphragm D into the ionizing chamber I, which is a brass cylinder about 40 centimetres long and 10 in diameter; this is filled with parallel gauze discs, the adjacent ones of which are insulated from each other, while alternate ones are connected together. One set

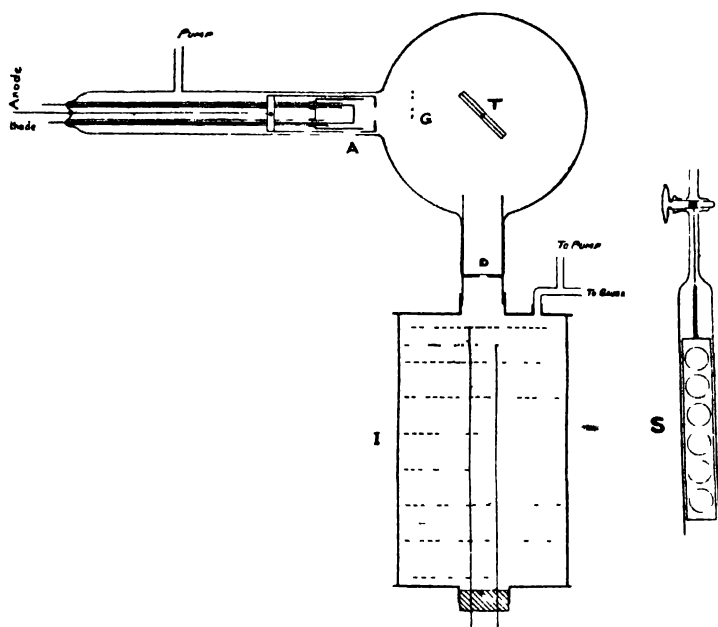


FIG. 1.

of discs is connected with one quadrant of a Dolezalck electrometer, the other set to one of the poles of a battery of about 600 volts; the other pole of this battery is put to earth. If the quadrant of the Dolezalck is originally put to earth, then on making the connection the current flowing into the quadrant will measure the ionization in I, and therefore the energy and the rays. To determine the character of the rays, screens of metal foil are inserted between the diaphragm and the ionizing chamber by means of the arrangement T. This is a holder soldered on to the tube just behind the diaphragm, inside this a metal plate pierced with a series of holes, one of which is empty

and the other filled with the different specimens of foil; this plate is raised or lowered by the windlass W, which winds up a piece of silk fastened to the plate. In some experiments the diaphragm itself was used as a target, the cathode being put opposite the diaphragm. This foil of various kinds was fixed in front of the diaphragm; and in this way the impact of cathode rays against different materials could be investigated.

In this method the energy of the rays is measured by the ionization they produce in the chamber. To absorb all the radiation it is necessary to have the gas in this chamber at a higher pressure than is admissible in the tube where the cathode rays are produced; the chambers must therefore be separated by a diaphragm which can stand a difference in pressure of some millimetres of mercury and yet be thin enough to allow the rays to pass through them. As these rays are extremely easily absorbed this necessitates the use of diaphragms which are less than a thousandth of a millimetre in thickness. Considerable difficulty was found in getting diaphragms to satisfy these conditions; the method finally adopted is due to my assistant, Mr. Everett, and consists in putting a drop of a solution of celluloid in amyl-acetate on the top of mercury in a shallow vessel. As the solution evaporates a thin film of celluloid is found on the mercury, and this is allowed to get thoroughly dry before being removed. By this device the boundary is free while the film is drying; if it is fixed the film tears from the shrinkage which takes place while it is drying.

I will now consider some of the results obtained by this method, and will first take the change in the absorption of the rays by a layer of aluminium, gold-leaf, or silver as the energy of the cathode rays producing the Röntgen radiation is gradually increased. We know that, speaking generally, hard rays correspond to large energy, soft rays to small, and it might be thought that as we increased the energy we should get a fairly constant rate of increase in the proportion of the radiation getting through the foil. When we try the experiment we find, however, that the increase in the transmissibility of the Röntgen rays with the energy of the parent cathode rays is not of this uniform character. The graph representing the relation between the absorption of the Röntgen rays and the energy of the cathode rays much more nearly resembles a series of steps with flat places between them than a uniform slope. Great changes in the energy of the cathode rays may give rise to very small ones in the absorption of the Röntgen rays they produce, as the absorption fixes the character of the Röntgen rays; this shows that this has altered but little in spite of the large alteration in the energy of the cathode rays. This is illustrated by the following Table, which gives the absorption produced by the same pieces of foil when the voltage of the cathode rays is steadily increased; the numbers given represent the ratio of the energy in the rays before and after they pass through

the foil. The target struck by the cathode rays was silver in the first Table, aluminium in the second

TABLE I

Voltage of Cathode Rays	Absorption				Celluloid
	Gold Leaf	Aluminium Foil	Copper Foil	Silver Foil	
700	10	60	96	15	6
800	10	70	40	15	6 6
900	10	50	36	13 5	7 2
1100	11	54	42	16	7
1250	10 8	51	36	13	7 2
1500	10	30	34	12 4	7
2000	10	20	26	10	6
2500	8	15	22	8	6
3000	8 1	10	17	7	6 5
3500	4 4	4 5	7 9	3 7	4
4000	4	3 6	6	3 1	3

TABLE II

Voltage of Cathode Rays	Gold Leaf	Aluminium Foil	Copper Foil	Silver	Celluloid
700	10	6	11	9	9
800	8	5	9	4 2	8
900	8	4	5	3 9	7
1000	6	3 3	4 5	3 1	8
1100	6	3	4	2 5	7
1300	4 8		4		5 6
1400	3	3 2			
1500	4 8		3 7	1 85	5 6
2000	3	2 7	3 3	2	4 4
2200		1 9			
2500	1 8		3 2	1 4	2 6
3000	1 8	1 7	2 4	1 2	1 7
3500					
4000	1 75	1 6	2 6	1 1	1 9

Many other materials, such as lead, platinum, iron, quartz; and carbon, have been tried as targets, but whatever might be the nature of the target all the results showed the feature to which I have just drawn attention, the changes in the penetrating power of the Rontgen rays taking place for the most part by comparatively abrupt jumps at particular values of the energy of the cathode rays, while between these values the changes in the character of the

Röntgen rays produced by changes in the energy of the cathode rays are but slight.

This result has, I think, a very important bearing on the origin of Röntgen rays. If these rays were in the main produced directly by the stoppage of cathode rays, we should expect the quality of the Röntgen rays to vary *pari passu* with the energy of the cathode rays. We have seen that this is not the case; the bulk of the rays seem to keep of approximately constant quality, in spite of wide variations in

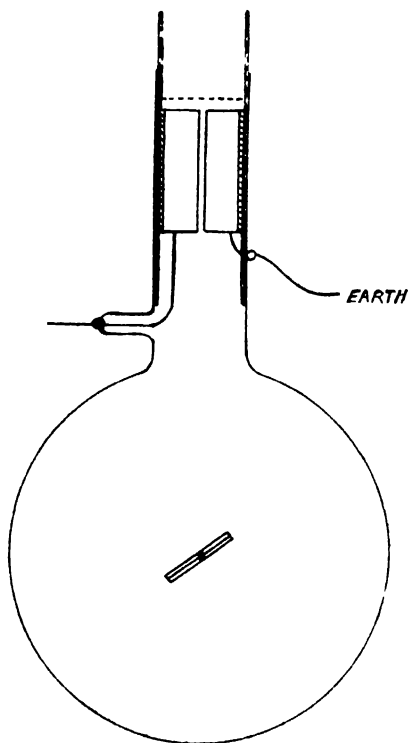


FIG. 2.

the energy of the cathode rays. This result seems to me to prove that the bulk of the Röntgen rays are produced indirectly and not directly by the cathode rays. I take the view that the most important part played by the cathode rays for this purpose is to ionize some of the atoms in the target, expelling electrons from these atoms, and that it is the subsequent return of electrons to ionized atoms which gives rise to the greater part of the Röntgen radiation; as long as

the type of ionization remains the same this process is independent of the energy in the cathode rays which produced the ionization. So that as long as a cathode ray has energy enough to ionize an atom in the target, it will produce Röntgen rays of the same type as those due to cathode rays with greater energy; it is only when the energy increases to such an extent that the cathode ray is able to produce a new type of ionization—to separate, for example, an electron from a ring of electrons nearer the centre of the atom, and not merely from the outside ring—that we should expect to find marked changes in the quality of the Röntgen radiation. When, however, the energy in the cathode ray reaches a critical value of this kind there will be a rapid change in the type of the Röntgen radiation. We should expect that these critical values would depend upon the material of which the target is made, and a reference to Tables I. and II. indicates that while the most marked change with a silver target takes place between 3000 and 3500 volts, with an aluminium target the change takes place at a smaller voltage, between 2000 and 2500. The type of radiation given out on this view is a “characteristic” radiation of the material of which the target is made. The voltages at which rapid changes in the absorption of the rays occur are those which are necessary to excite the various types of “characteristic radiation.”

I have made a considerable number of experiments on the character of the Röntgen rays emitted by different substances when bombarded by cathode rays of different velocity, measuring the absorption of the rays produced by different numbers of layers of aluminium foil. The absorption produced by the first layer is always very much greater than that produced by a second layer behind it, showing that the main part of the radiation is so soft as to be completely absorbed by one layer of the foil; when this very soft radiation is eliminated constant values of the absorption are obtained for considerable variation in the velocities of the cathode rays. It is the absorption by one layer of aluminium foil after the soft rays have been abstracted which is given in the following table: the rays were generated by cathode rays striking against celluloid, lead and aluminium targets respectively.

Energy of Cathode Rays expressed in Volts	Absorption by 1 Thickness of Aluminium Foil Target		
	Celluloid	Aluminium	Lead
800	4	1.6	2
1000	3.2	1.45	1.6
1200	3	1.3	1.4
1500	2.8	1.4	1.4
2000	2.5	1.2	1.2

There is thus considerable difference between the quality of the rays from the celluloid target and those from the lead and aluminium ones. There is little difference, however, between those from lead and aluminium for the higher voltages, nor did I find any very marked difference in the quality of the Röntgen rays produced when the same number of cathode rays of the same speed struck lead and aluminium targets respectively.

With rays of this very soft type it is only a very thin layer close to the surface of the target which is operative, and so the cleanliness of the surface is a matter of great importance. If different substances give out characteristic radiation of the kind produced by these slowly moving cathodes, we should expect that the absorption by these substances would show anomalies when the rays passing through them approached in type to their characteristic radiation, and that the ratio of the absorption of different substances would show considerable variation. This was a very marked feature in these experiments. If, for example, we compare the absorption of the rays by gold and aluminium, the absorption by aluminium for very soft rays—say for those corresponding to voltages of 400 or 500—is in comparison with gold many times greater than for rays corresponding to more than 1500, so much so that a piece of aluminium foil which does not absorb nearly so many of these harder rays as a piece of gold-leaf may absorb three or four times as many of the softer rays. The following examples show how marked is this effect; the plates of the different metals were not of the same thickness, so that the results do not give the absolute values of the absorption but only the variation of the absorption with the voltage; the target was silver.

Voltage of Cathode Rays	Absorption			
	Gold	Aluminium	Copper	Silver
300	7	40	40	4
550	7	40	16	6
1000	3.7	1.8	5	3

Thus with the highest voltage the absorption of the gold is twice that of the aluminium, while with the lowest it is only about one-sixth; this points to the existence of a soft aluminium characteristic radiation, and also probably to one for copper.

The next question I shall consider is the variation in the energy of the Röntgen radiation with that of the cathode rays which produce them. We must remember that in the method we are considering at present the Röntgen rays have to pass through a thin film of celluloid before their energy is measured, so that any energy absorbed

in the film would escape detection. In my experiments the Rontgen rays first became appreciable when the voltage on the cathode rays was about 150 volts—the limit depends on the thickness of the film, the magnitude of the stream of cathode rays, and the sensitiveness of the electrometer—it then increased comparatively slowly at first, but very rapidly when the voltage rose above a certain value. This value was in the neighbourhood of 350 to 400 ; it seemed to depend somewhat on the nature of the target. The energy in the Rontgen rays at different voltages, the number of cathode rays being kept constant, is shown below ; the target was made of celluloid :—

Voltage	Energy in Rontgen Rays	Voltage	Energy in Rontgen Rays
150	1	350	45
200	6	400	180
250	15	450	360
300	30		

The energy in the Rontgen rays does not continue to increase at this rate with the potential ; it attains a maximum at a certain voltage, and then, for a time at least, diminishes as the voltage increases. The potential for maximum voltage is subject to considerable variation ; the cause for this I have not yet had time to investigate ; the thickness of the film, the pressure in the cathode-ray tube seem both to affect this potential.

I now proceed to considering the other method of investigating the quality of the rays, i.e. by the velocity of the electrons ejected when the rays fall on a metal plate. To apply this method, the ionizing chamber I used in the previous one was replaced by a sphere silvered on the inside. At the centre of the sphere there was an insulated metal plate connected with one pair of quadrants of a Dolezalek electrometer. When the rays fall on this plate electrons are given off, and the plate acquires a positive charge which is registered by the electrometer. If the energy with which the electrons are ejected is measured by V volts, then if the silvered surface of the sphere is made negative to the plate by V volts or more, the electrons cannot escape from the plate and the electrometer will not be affected by the incidence of the rays. In this method it is desirable to have the pressure of the gas in the bulb as low as possible, so that no diaphragm between the cathode ray tube is necessary, and thus the rays which may be absorbed by the diaphragm and escape detection by the first method will be registered by this. On the other hand, since the diaphragm prevents charges of electricity which would vitiate the measurements from passing from the cathode ray tube to the parts connected with the electrometer, it is necessary to introduce some means for stopping these charges. This was effected by having in the tube, between the cathode ray tube and the silvered sphere, two half-cylinders insulated from each other and

connected with the poles of a 600-volt battery ; everything going from one tube to the other had to pass between these cylinders, and if it were electrified would be driven on to one or the other. The experiments with this method, which are not yet completed, give results which agree with those obtained by the other. They show that a potential difference of a few volts between the silvered sphere and the metal plate is sufficient to stop the vast majority of the electrons, even though the cathode rays had fallen through many hundred volts, and that as before the character of the Röntgen rays

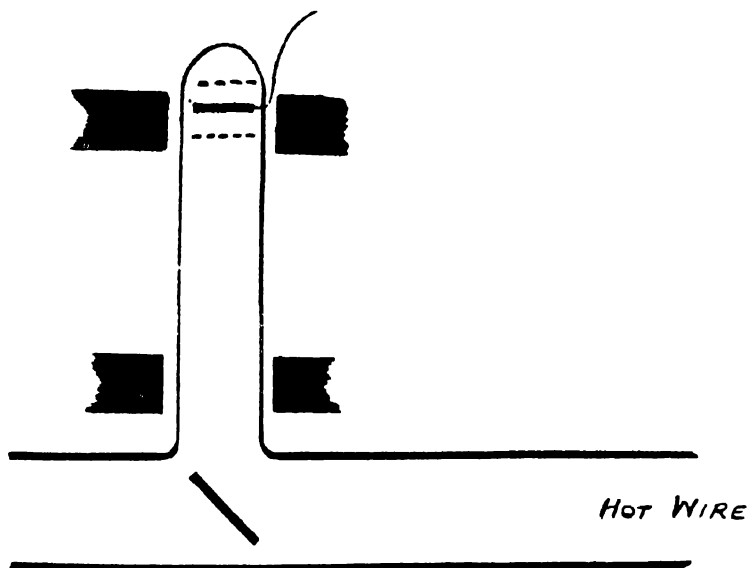


FIG. 3.

only changed slowly with the energy of the cathode rays. Thus when 1000 volts cathode rays fall on a target the Röntgen rays produced are for the most part no harder than might be produced by 100 volt rays. The proportion of rays corresponding to anything approaching 1000 volts is so small that I have not yet succeeded in finding by this method any trace of their existence. I hope, however, in less strenuous times, when research, which can now only be an occasional relaxation, may become again one's main occupation, to carry out more elaborate experiments on this and other points of interest in connection with these rays.

[J. J. T.]

Friday, May 26, 1916.

SIR WILLIAM PHIPSON BEALE, Bart, K.C. M.P. F.C.S.
Vice-President, in the Chair.

PROFESSOR C. G. BARKLA, M.A. D.Sc. F.R.S.

X-Rays, Atomic Structure, Electromagnetic Radiation.

[ABSTRACT.]

I PROPOSE to give an outline, not of the properties of Rontgen radiation in general—that would be too large a task—but only of some of those properties which have an obvious bearing on two of the most important and the most fascinating problems in Physical Science—the problems of atomic structure and of electromagnetic radiation, particularly of X-radiation.

Before Sir Joseph Thomson's discovery of the electron, that is, of small particles of electricity freed from ordinary matter, it had been generally assumed that all bodies contained equal quantities of positive and negative electricity, which just neutralised each other. The process of electrification of any body was simply a process by which the body was given an excess of one kind of electricity or the other. Thomson's experiments showed that in a space relatively free from ordinary matter (the space inside a highly exhausted discharge tube) these particles could be obtained free, whatever the gas inside the tube and whatever the nature of the electrodes conveying electricity to and from the gas.

Since these early experiments, electrons have been obtained from matter by very different methods—by (1) heating; (2) bombardment by swiftly moving small particles as α and β rays; (3) exposure to light, especially of short wave-length; (4) exposure to X-rays; and (5) they are spontaneously emitted by substances we call radioactive substances.

In some of these cases the supply of electrons is largely dependent on the presence of other substances, or is influenced by surface conditions, while radioactive processes have only been observed in a limited number of elements. Perhaps the most convincing proof that electrons are not obtained from an impurity common to all substances, or that they do not reside simply on the surfaces of atoms, is that the number emitted from a substance exposed to X-rays is an atomic property unaffected by physical conditions or

even by chemical combination, and it can be foretold for an element if we know its atomic weight, or, more accurately, its atomic number.

Further, we can by X-rays get electrons from the *interior* without permanently affecting the stability of an atom.

We can, as I shall show, find the *number* of electrons in the atom; we can divide these into groups at different depths within the atom, and compare their properties—properties of course depending on their position and state within the atom.

Let us indicate methods of studying the electrons emitted by substances exposed to Röntgen radiation in the form of the secondary corpuscular radiation.

Precise measurements upon the corpuscular (electronic) radiation emitted by substances exposed to X-rays may be made by various methods:—

(a) By exposing a substance in an evacuated chamber to X-rays the magnetic deflection of the emitted particles may be observed much as in Thomson's experiment on Kathode Rays. Such measurements were made by Innes, and, assuming a value for e/m , the velocity was obtained.

(b) Observations, as by Townsend, of the variation of ionisation between two parallel plates with their distance apart, when one or both plates is exposed to X-rays, show the maximum distance traversed by the particles in air or any other gas. (The plates may be kept fixed and the pressure of the gas varied.) From Whiddington's Law, connecting length of path d and initial velocity v , i.e. $v^2 = ad$ when a is a known constant, the maximum velocity of emission may be determined.

(c) By C. T. R. Wilson's condensation experiments the tracks may be seen and measured, and the velocity of the electrons deduced.

(d) As all X-ray ionisation is by the swiftly moving electrons (secondary corpuscular radiation), determinations of the number of electrons emitted by a gas may be made from observations on the ionisation in the gas. From relative ionisations we can get relative numbers of ejected electrons (Barkla, Phil. Trans. A, v. 217, pp. 315-360), and from measurement of the saturation current and a knowledge of the number of ions produced per electron ejected it is possible to get the absolute number of electrons produced by a given beam.

Such experiments give us the number and velocity of electrons expelled by X-rays, and show us how few these are in comparison with the whole number of atoms traversed by the radiation. They show us that the negative electron is a constituent of all matter, but give us no idea of the total number of electrons in an atom.

On the other hand, positive electricity, which must also be a constituent of all matter, has never been obtained in a form which shows it to be free or entirely distinct from matter as ordinarily known. Thus in an evacuated tube the least massive positive

particles have been found to possess the mass of the atom of hydrogen; positive particles are not set free either by light or by X-rays; even when liberated in radioactive processes they are atoms of helium.

Positive electricity is thus much more securely fixed in matter. For these and other reasons, Kelvin suggested, and J. J. Thomson developed, the idea that an atom was built up of a uniform sphere of positive electricity with a large number of negative electrons. As the more diffusely distributed a charge is the less is its mass, such a charge would possess little mass—approximately the whole mass of the atom would reside in the electrons. It was therefore necessary to assume a large number of these, say 1700 per atom of hydrogen, and they were supposed to be arranged in rings or shells revolving round the centre of the atom.

It is on this point as to the number of electrons per atom that X-radiation phenomena afford most valuable evidence.

When X-rays are incident on matter, the matter itself emits X-radiations (secondary X-radiations). I have found the secondary X-radiations are made up of radiations of two types, which I have called (*a*) scattered X-radiation, and (*b*) fluorescent (characteristic) X-radiation.

The principal secondary radiation, proceeding from light elements exposed to a primary X-radiation, is a radiation of the same wavelength and the same penetrating power. From observation of the character and intensity of this scattered radiation, I concluded that per electrons in matter were the scatterers, and that the scattering the atom (consequently the number of electrons per atom), for light atoms at least, was proportional to the atomic weight.

J. J. Thomson stated this more precisely by pointing out that each charged particle, when under the influence of the primary X-radiation, is acted upon by the varying electric field, is moved by that field, and so sends out a wave-motion along its own tubes of force. This wave-motion is the scattered radiation.

From measurements of the intensity of radiation scattered applied to J. J. Thomson's calculated value for the energy of a beam lost by scattering from ions (the fraction lost per cm. of path = $\frac{8\pi}{3} N \frac{e^4}{m^2} \mu^2$)

I found, with data available, there were about 200 electrons per molecule of air. Applying more recent and exact data, we find approximately $14.5 \times (2.75 \times 10^{10})$ electrons per c.c. of air under standard conditions.

This and the corresponding measurements for scattering by other substances indicates 7 electrons per atom of N, 8 for O, 6 for C, 16 for S, 1 for H. It is remarkable that the determined number of electrons is as near to 7 for an atom of nitrogen as it is possible to estimate the pressure of the air upon which the experiments were made.

At about the same time as the announcement of these corrected values, Rutherford from experiments on the scattering of α particles arrived at a conclusion which is complementary to this. He concluded that the deflections of α particles observed are not such as could be explained either by the electrons or the diffuse positive charge in the atom. He showed it was necessary to replace the diffuse positive charge by a very concentrated positive charge, and found for it a value approximately equal to half the atomic weight times the charge of an electron, i.e. $\frac{1}{2} e$. This just agrees—though the measurements did not permit of equal accuracy—with the $\frac{1}{2}$ electrons with charge $-e$. The two are complementary and give us a neutral atom.

Later work by Moseley on the spectra of the elements given by interference phenomena with X-rays has further supported this conclusion, by showing equal steps between the spectrum of each atom and that of the next in the periodic series, each step roughly corresponding to an increase in the atomic weight by two units.

Bohr has extended the theory to account for the line spectra of light elements.

This, then, is the structure which at present perhaps finds greatest acceptance—a very small nuclear positive charge of unknown but probably quite complicated structure surrounded by a number of electrons at various distances from the centre; the positive nucleus having a charge approximately equal to half the atomic weight times the charge of an electron (e), now more accurately expressed as the atomic number (n) times (e); the number of negative electrons outside the nucleus being approximately half the atomic weight, or, more accurately, equal to the atomic number.

It is evident that a great burden is placed on the solitary electron which with the positive nucleus constitutes a hydrogen atom. To get over the difficulty Bohr has suggested that the electron may be in one of many distinct orbits. The normal hydrogen atom is supposed to have a diameter 1.1×10^{-8} cm., but according to Bohr's theory it also may be 4, 9, 16, 25 times this, and to explain stellar spectra must be 1.2×10^{-5} cm. in diameter.

Writing of this theory Jeans says "it explains so many facts, and the numerical agreement with observation is so complete, that little doubt will be felt that it is at least based on a very substantial substratum of truth."

Before proceeding to explain how we can get further information of the atoms from X-ray experiments, let us look at the *theory of scattered radiation* which enabled us to calculate the number of electrons. It is briefly this: The primary waves spread in all directions from the anti-kathode of an X-ray tube and influence every electron in the matter through which they pass. Whatever the

normal motion of an electron may be, this produces no appreciable X-radiation ; but the perturbations produced by the primary radiation set up a wave motion along the tubes of force which extend from the electrons in all directions. This radiation from the electrons is called the scattered radiation. It is really a radiation from electrons moved by the primary radiation, and in fact always controlled (so far as the motion producing radiation is concerned) by the primary radiation.

The evidence in support of the fundamental truth of this theory, such as the quality, polarisation, distribution and intensity of the scattered radiation, is so overwhelming that it cannot be questioned. But many of the experimental results, as polarisation and distribution, may be reproduced by transverse wave motion along strings, and only really prove the electromagnetic radiation to be a transverse wave motion. They do not indicate whether the waves are localised and proceed along definite paths or tubes, or whether they spread out in spherical shells. But this is an important question in view of what has been called the quantum theory of radiation, suggesting that radiation occurs in definite units of energy.

According to this theory of light, X-rays, etc.—in fact, of what is called electromagnetic radiation in general—radiation is made up of definite units or bundles, each bundle containing an amount of energy E proportional to the frequency n of the radiation with which it is associated. Thus $E = hn$, where h = Planck's constant.

But when we see the results of the old spreading wave theory giving for the number of electrons in a c.c. of air under standard conditions a value $14.5 \times 2.75 \times 10^{19}$ (i.e. an average of 14.5 electrons per molecule), and when we think that *a priori* there was no reason why it should not be 1000 times this or $\frac{1}{1000}$ of this, we cannot but conclude that this theory is not only adequate, but that it would be exceedingly difficult to supersede.

[If we imagined that ions were the scatterers, the calculation would give 1,000,000 times more ions than molecules present, or trillions times the actual number.]

This is really most remarkable confirmation of the older electromagnetic theory of radiation. It can mean nothing else than that the process is a continuous process, radiation being emitted in any quantity, however small. There is not only no suggestion of a quantum or entity in radiation, but these phenomena of scattering become absolutely meaningless on any such theory.

This, however, is only one of the facts obtained from experiments on the scattering of X-rays that support the theory : the whole body of evidence is remarkably strong.

But close though the agreement is, the simple theory does not seem sufficient to explain all X-ray phenomena. The result of many experiments suggest that the process of radiation is a discontinuous process, that it does not take place steadily but in a jerky fashion, and that radiation and absorption must, as I have said, be in definite

units of energy. For instance, the velocity of electrons ejected by X-rays is independent of the intensity of the radiation; it depends only on the wave-length (or frequency), being given by $\frac{1}{2}mv^2 = hn$ from any substance.

This certainly looks as if the radiation consists of indivisible bundles of energy—as though these were totally absorbed or not at all absorbed.

It has also been shown by Beatty and others that when X-rays are produced, radiation of a given wave-length is only emitted by an anti-kathode when the generating kathode particles have a velocity v greater than that given by $\frac{1}{2}mv^2 = hu$.

On the other hand, the phenomena of scattering suggest—in my opinion, prove—that the emission and absorption of X-rays take place in any quantity whatever. It is the phenomena of the transformation of energy from that of moving electrons into X-radiation and from X-radiation into corpuscular radiation that suggests “quanta” of radiation.

These newly discovered facts concerning radiation have not yet been made to fall in completely with the older theory, but attempts are being made to reconcile them as far as possible, and I have quite recently got some most suggestive experimental data on the subject, which I will briefly explain.

Each element under suitable stimulus emits characteristic X-radiations, that is, radiations of wave-length characteristic of the element. The total characteristic radiation of an element thus gives a line spectrum consisting of several widely separated groups of neighbouring lines. These various groups are the J, K, L and M radiations.

To excite one of these groups of radiations, say the K radiation, it is essential that the primary beam be of shorter wave-length than the constituent of shortest wave-length.

It can be simply shown from the variation of absorption in an element with the wave-length of the primary radiation, that certain portions of the absorption are definitely associated with the emission of each group of characteristic radiations. Thus there is the K absorption associated with the emission of K fluorescent characteristic radiation; L absorption associated with the emission of L characteristic radiation; etc.

Similarly we can show that the whole secondary corpuscular radiation emitted by a substance can be divided into groups, each associated with the emission of a particular fluorescent characteristic X-radiation. Thus the three phenomena of absorption of primary radiation, emission of secondary corpuscular radiation, and emission of fluorescent characteristic X-radiation occur together. We have K absorption, K secondary corpuscular radiation, K fluorescent characteristic X-radiation; L absorption, L secondary corpuscular radiation, and L fluorescent characteristic X-radiation; etc.

From measurements of the energy absorbed and the energy re-emitted as corpuscular and as fluorescent characteristic X-radiations, certain very important conclusions may be drawn. The significance of the results is most easily understood if we express them approximately. [Energy has been measured by the ionization method.]

Let the wave-length of the primary radiation be λ and that of the K fluorescent characteristic radiation of the substance bromine be λ_K . Then when λ is greater than λ_K , for a given absorption of the primary radiation the same number of electrons is emitted by bromine (L, M, N, etc., electrons) as by air (K, L, M, N, etc., electrons). When λ is just less than λ_K the additional K absorption in bromine is accompanied by the emission of only half as many electrons, that is, only half the K energy absorbed is re-emitted as energy of K corpuscular radiation. But as λ becomes smaller, an increasing fraction of the energy absorbed (K absorption) goes into the K corpuscular radiation. And the rate of change indicates that with a primary radiation of very small wave-length practically the whole of the K absorption would be accounted for by the K corpuscular radiation alone. There is in addition very strong indirect evidence that when λ is very small nearly all the energy absorbed is re-emitted as corpuscular radiation, for whatever the absorbing substance under these conditions the energy of this corpuscular radiation is approximately a constant.

Also when the wave-length λ of the primary radiation is just less than that λ_K of the fluorescent X-radiation, of the energy specially absorbed in association with the emission of the fluorescent radiation (K absorption) nearly 0.5 is re-emitted as fluorescent X-radiation. As λ becomes less the fraction diminishes almost proportionately until for primary radiation of very small wave-length the energy of the fluorescent radiation becomes a very small fraction of the energy of the primary radiation specially absorbed. It is evident at once that the energy of K fluorescent X-radiation from bromine is approximately complementary to that of the K corpuscular radiation. From the study of these relations we find:—

The energy of primary radiation absorbed to expel one K electron is greater than that required to expel one L electron, by a quantum of the K radiation. We then naturally consider the K electron to be nearer the centre of the atom, and conclude that in general the electrons associated with the higher frequency X-radiations are nearer to the centre than those associated with lower frequency radiations. Thus J, K, L and M electrons are arranged in this order from the centre outwards.

As both K and L electrons leave the atom with the same velocity—this has been recently demonstrated—we may express the fact in this way: A quantum of K radiation is the energy required to move an electron from the position and state of a K electron to the position

and state of an L electron; by analogy it may be concluded that a quantum of L radiation is the energy required to move an electron from the position and state of an L electron to the position and state of an M electron.

We also find a quantum of K radiation is emitted for each K electron ejected, as shown in the Table:—

Approximate wave length of primary λ radiation.	Number of quanta of K fluorescent radiation emitted per K electron ejected.
0.87×10^{-8} cm	1.09
0.71×10^{-8} "	0.95
0.56×10^{-8} "	0.85
0.49×10^{-8} "	0.81
0.35×10^{-8} "	0.90

With primary radiation of just shorter wave-length than that of the K radiation, for each electron emitted there is absorbed the energy of a quantum of K radiation as well as that carried away by the electron; therefore *each absorbing atom has absorbed about two quanta of primary radiation*. As λ decreases, the energy absorbed by each atom is that of one quantum of primary radiation (going to an electron) plus the energy of one quantum of secondary characteristic radiation (going to the fluorescent characteristic radiation). This varies from the energy of two quanta to that of one quantum of the primary radiation as the wave-length diminishes. Absorption, therefore, is not in whole quanta.

There is thus again no evidence of an entity or indivisible quantum of radiation even in the phenomena supposed to strongly support such a theory. The reason why it has usually been supposed that energy is absorbed in quanta is that the second part is frequently small; it may, however, be any fraction of another quantum of primary radiation.

We have shown that the emission of each electron of the corpuscular radiation is associated with the emission of a quantum of the corresponding fluorescent X-radiation, but there is conclusive evidence that the electron, after emission, takes no part in the phenomenon of fluorescence—that is, the emission of characteristic radiation is entirely independent of the electrons after their emission. We must, therefore, conclude that the atom which emits an electron emits also a fluorescent radiation characteristic of the atom itself. The observed relations lead to the following considerations:—

When a K electron is hurled out of the atom it is possible that for stability another electron must fall into the position and state of the K electron. If it falls from the position and state of an L electron, the excess energy, which is that of a quantum of K radia-

tion, must be re-emitted. The emission of a quantum of K radiation for each electron expelled we have found to be an experimental fact. By analogy the energy of a quantum of L radiation will presumably be emitted when an electron falls from the position and state of a lower frequency electron to the position and state of the displaced L electron.

It is possible that there are not electrons of every series in every atom of the same substance, or, if there are, they may not be in the best position to enable them to replace an electron of an adjacent higher series. If, for instance, a K electron were ejected from an atom which did not contain an L electron, or in which the L electron was situated on the other side of the centre, its place might be taken by an M electron, with the result that the energy emitted as characteristic radiation would be equal to that of one quantum of K radiation + one quantum of L radiation. This would be equal to one quantum of radiation of slightly greater frequency than what we have previously regarded as the principal component of the K radiation, and might account for a neighbouring higher frequency spectral line in the K radiation, as was suggested by Kossel.

Whatever the exact process of emission of the fluorescent characteristic radiations, the experiments described above lead to the conclusion that a characteristic radiation (of series K, say) is probably emitted when an outer electron falls into the position of a displaced K electron, the energy previously absorbed in displacing the K electron in excess of that carried away as kinetic energy being now re-emitted as a quantum of K radiation, or, what seems more probable, as a quantum of K radiation accompanied by quanta of lower frequency radiations, due to successive falls of electrons between the outer rings.

In conclusion, it seems absolutely certain that electric radiation can be and is both emitted and absorbed in quantities which are not multiples of any particular unit; that radiation even by individual electrons is in many cases a continuous phenomenon. But that in certain processes within the atom—probably when an electron falls from one ring to another—the phenomenon takes place in a very definite manner, involving the radiation of a definite amount of energy which is proportional to the frequency of vibration.

Though there are many problems of absorption and radiation still awaiting solution, as indeed there always must be, the difficulties seem to be definitely shifting from the radiation itself to the structure of the atom and to processes taking place within the atom. The evidence obtained from experiments on X-rays indicates that there is no such thing as a quantum of radiation in the sense in which it has been frequently used. There is no entity apart from the atom. The structure of the atom only permits of the true absorption of a quantum of energy, and when the original configuration is reached it re-emits that quantum.

It may be briefly added that the evidence suggests that mere

collision of electrons with an anti-kathode is not of sufficiently sudden a nature or sufficiently violent to result in the generation of X-rays as ordinarily detected. The probability is rather that the function of the kathode particle is to displace electrons from atoms in the anti-kathode, and thus to produce vibrations in the atoms which result in the emission of the primary X-radiation. Some of these vibrations may be due to the fall of electrons from definite positions—outer rings—in which case characteristic radiations are emitted; or they may be due to falls from any other positions, in which case the radiation is not characteristic of the anti-kathode. Such a mixture of radiations has been observed.

[C. G. B.]

Friday, January 16, 1920.

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Fullerian Professor of Chemistry.

Low Temperature Studies.

IN 1906* it was pointed out that a workable thermoscope could be constructed by taking advantage of the fact that charcoal saturated with air or other gases at a low temperature is very sensitive to radiant energy, and that the small increase of temperature produced in a 1 gramme bulb of charcoal by the approach of a candle flame expels sufficient gas to move a suitable index. As the response was obtained even though, in the forms of apparatus then employed (Fig. 1), the radiation had to traverse several thicknesses of glass before reaching the charcoal, it was inferred that a still more sensitive thermoscope could be constructed if the receptacle containing the charcoal were closed by a thin membrane of stretched india-rubber, which is more transparent to heat than glass. Such a membrane being practically impervious to most gases at low temperatures,† it appeared possible to make the receptacle air-tight.

This arrangement was tried with the charcoal in a metal capsule covered with a very thin clear membrane, as described in the diffusion experiments of 1915.‡ The tube from this cell led to a small liquid manometer. The cell was immersed in liquid air with the clear membrane directed vertically upwards, and the charcoal was allowed to saturate with clean air up to atmospheric pressure. Covering the membrane was a light metal shutter. When everything had become equilibrated, the shutter was lifted, thus exposing the cell to radiation from any source above and in line with the neck of the silvered vacuum vessel. With a Leslie cube at room temperature as source, an immediate response was obtained, sufficient to displace the index of the manometer to the limit of its scale in a few minutes. On replacing the shutter the opposite effect was obtained, as the charcoal re-absorbed the gas displaced by the dark radiation.

In addition to rubber membranes, plates of rolled silver chloride

* Proc. Roy. Inst., xviii. p. 445.

† Proc. Roy. Inst., xvii. p. 424; xxi. pp. 558, 816.

‡ Proc. Roy. Inst., xxi. p. 558.

free space was by smearing the interior surface of a glass box with glycerine, closing and allowing it to stand for a few days, when the dust settled, adhering to the glycerine. On applying the light beam test the box was found to be what Tyndall termed "optically empty." Aitken has devised an apparatus for counting the particles in the air, suggested by experiments on cloud condensation due to the cold produced by sudden expansion of air saturated with water vapour. Very briefly his method is to make these solid particles the nuclei of small rain-drops, which can then be counted. Ordinary London air contains about 100,000 suspended particles, organic and inorganic, per cubic centimetre. The particles get coated with all kinds of adherent organic matter which, coming in contact with the bubble, affects its surface tension locally, thereby inducing instability.

When bubbles blown with pure air were formed in vessels closed to prevent communication with the outside air, it was soon recognised that, when the interior of the vessel had become free from suspended matter by long standing and deposition on the walls the surface of which was coated with glycerine soap solution, the bubbles lasted much longer.

The methods of purification employed for the purpose of obtaining long-lived soap bubbles were (1) simple displacement by purified air; (2) deposition of the solid material by electrical discharge in the space to be utilised. To demonstrate the two methods, domed glass shades about 2 ft. high were used, each with a black wood base, in which was a circular glass window. A concentrated beam of light from an arc lamp was reflected up through the window, thus strongly illuminating the solid impurities in the air-space enclosed by the shade. Highly compressed air from an ordinary steel bottle, purified by passing it through three small glass towers containing, respectively, soda, lime, and cotton-wool damped with glycerine, was introduced in the bottom of the shade through holes in a circle of lead pipe secured on its wooden base. In about a minute the beam disappeared as the impure air was swept out through a small hole in the top of the shade. To show the electrical method of purification a similarly fitted shade had an insulated steel point hung within it from the centre of the dome. This was connected to one pole of a Wimshurst machine, while the other was earthed along with the lead pipe described above. Within two minutes of starting the point-discharge the illuminated cloud had practically disappeared. When this treatment was applied to a vessel containing soap solution, a heavy mist of large floating water particles first appeared, of some persistence.

BUBBLES FROM THE EVAPORATION OF LIQUID AIR.

The evaporation of liquid air readily affords a supply of pure mixed oxygen and nitrogen. Apparatus for this purpose is shown in

Fig 1. The liquid air is contained in a tube A, which is fitted by a ground cap to the delivery tube B, and placed in a vacuum vessel D to control heat influx. At B one branch tube leads to the thistle-shaped funnel from which the bubble is to be suspended, while another branch leads to the stop-cock C, by means of which the admission of air into the bubble can be regulated. The cavity above the ground cap, and the horizontal tube leading to the bubble are packed with copper-wire gauze in order to warm the air evaporated.

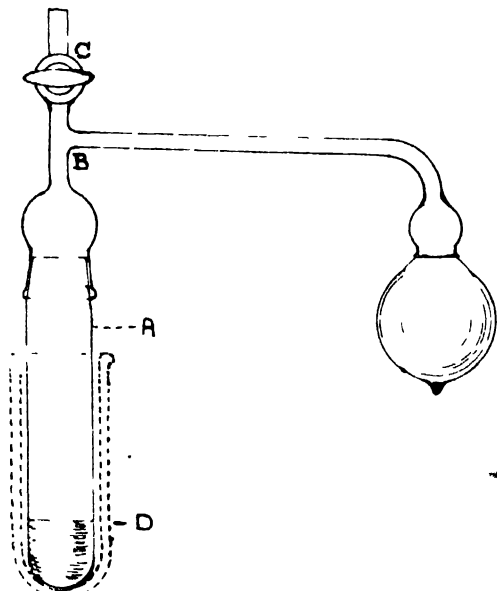


FIG. 1.

The soap solution is supplied to the mouth of the thistle-shaped funnel in the usual way: or otherwise, by having a constriction in the tube above the thistle-shaped funnel, together with a stoppered dropping funnel. It is thus possible to fill the constriction with soap solution, and develop bubbles singly or in succession, as desired.

APPARATUS FOR THE PRODUCTION OF BUBBLES UNDER VARIOUS PRESSURES.

The apparatus, Fig. 2, is a spherical glass flask A of $2\frac{1}{2}$ litres capacity, fitted with an india-rubber cork which has been previously cut and steamed in order to remove volatile organic matter. The

tube B leads from the vessel A to a mercury U-tube manometer, and to the stop-cock to which the air-pump is attached; while another tube carries at its lower end the constriction C and the funnel on which the bubble is to be formed, and at the upper end the small reservoir G of soap solution. Air passing through the purifying bulbs F is admitted by the regulating stop-cock D, through the reservoir G to the funnel-mouth C. A capillary tube between D and G assists in the control of air when the pressure in A is very small. By slightly tilting a few drops of the solution in G down the tube to C, bubbles are easily blown within the flask A, even at a pressure less than 1 mm. Hg. At this pressure the contraction of the bubble proceeded visibly, and was accelerated as the diameter was reduced.

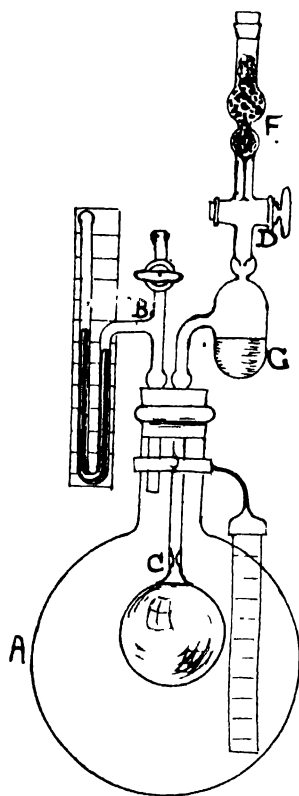


FIG. 2

In Fig. 3 various forms of bubble-support tubes are shown, convenient for different purposes: (a) permits the insertion of a long fine tube or rod into the bubble; (b) allows the apparatus to be inverted, without loss of soap solution, so as to have the bubble supported from below; (c) permits the formation of bubbles in otherwise inaccessible places (this form has a dropping funnel and stop-cock attachment to the reservoir); (d) is useful for forming a succession of bubbles (by a series of slight regulated jerks of the reservoir, a series of films form in its exit-tube, which pass down to the thistle-shaped funnel, and there produce a chain of bubbles).

An ordinary tubulated aspirator, of about 12 litres capacity, is very convenient for the study of bubbles up to nearly 20 cm. in diameter. For careful measurements a plane-sided vessel is necessary to prevent optical distortion. For this purpose a metal-framed plate glass box, 1 foot length of side, was used. The sheet of glass forming the top was nearly 6 mm. thick; it was pierced with three or four holes from $\frac{1}{2}$ cm. to 3 cm. diameter, besides the central hole, 3 cm. in diameter, for supporting the blowing tube. These extra holes allow the

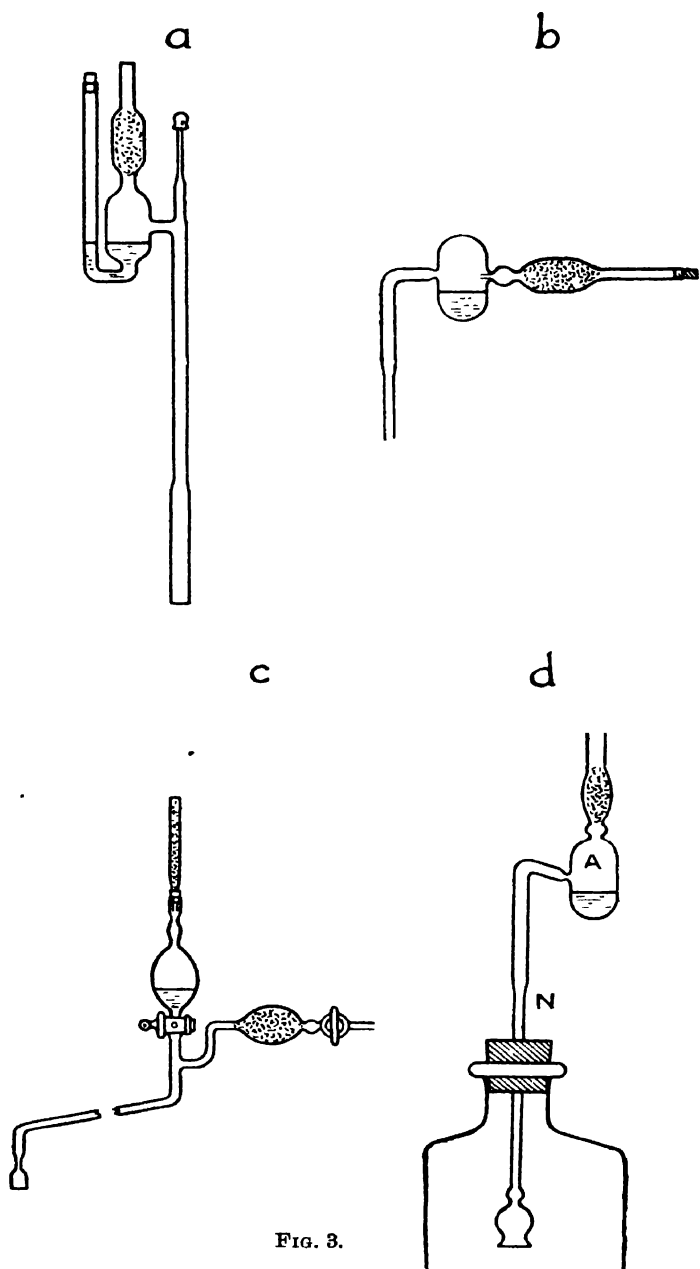


FIG. 3.

admission of flexible glass supporting rings, or draining points, where necessary. Thus, by means of the dropper, Fig. 3a, a fine glass thread or wire can be passed down through the bubble, so that the drop is removed and the distortion observed. Similarly, through one of the openings in the lid of the cubical glass chamber, a thin glass rod with an up-turned end, approaching the bubble from below, can be employed to drain off any excess of liquid, and thereafter to determine the changes effected in the vertical and horizontal diameters.

DISTORTION OF BUBBLES, HANGING OR SUPPORTED.

The following instances show the amount of distortion or ellipticity, present in hanging bubbles, under different conditions :—

A bubble, 19.1 cm. vertical diameter, 17.8 cm. horizontal diameter (ellipticity 7 per cent.), when freshly blown from solution of 5 per cent. potassium oleate, 50 per cent. glycerine, was only feebly coloured, and therefore fairly thick. On the fourth day its vertical diameter was 18.1 cm., and on fifth day 17.7 cm., being then sufficiently thinned to be well coloured.

A bubble of 5 per cent. ammonium oleate in 50 per cent. glycerine, measuring 17.25 cm. vertically and 16.2 cm. horizontally (ellipticity 6 per cent.), was at first only feebly coloured in the lower one-fourth. By the third day the vertical diameter was reduced to 16.6 cm. from the reduction of mass, shown by an intensification of the colouring. A bubble of this composition exposed to water vapour, by running water into the containing vessel, will condense and absorb the water vapour and become thickened again for a time. Such a bubble of 30 cm. vertical diameter was dragged down by the water it absorbed in one day to 31.8 cm., an elongation of 6 per cent.

A bubble, 11.2 cm. diameter, with the upper half black and lower half coloured, was reduced to 10 cm. diameter, when entirely black, by drainage—i.e. a distortion of 12 per cent. vertically was caused by the lower half of a thin black bubble thickening to show colour by adding a few drops of soap solution.

If instead of the bubble being supported from above it rests on a suitable light ring support, it will obviously decrease in vertical diameter when it becomes thickened and weighted. This was frequently observed with bubbles of about 40 cm. diameter, resting on a 10 to 12-cm. ring of thin iron wire.

With a water layer in the globe, considerable variations were noted from day to day, e.g.:-

Thus, a bubble coloured green and carmine, very brilliant but fairly thick, 42.6 cm. diameter, thinned to half black and half silvery (next thicker colour to black), 43.6 cm. diameter.

Another bubble coloured amber to purple, near lower limit of

thickness to show colour, 22.7 cm. diameter, thinned to all black (thinnest possible), 23 cm. diameter.

A coloured bubble 43.8 cm. diameter, thickened in 15 minutes by condensation to 42.7 cm. diameter.

Bubbles of such a size flattened down on their supporting rings as they became thicker and heavier, and could be seen hanging over the ring-support from this cause.

A bubble 39 cm. diameter, hanging from a 4-cm. glass funnel support, thinned to over 70 per cent. black on its second day, and increased until its 63rd day, when it burst, 80 per cent. black. On five occasions a slowly accumulated drop was observed to fall off—namely, on the 6th, 10th, 20th, 27th, and 52nd days respectively. The alterations in diameter which thereupon resulted were as follow:—

With drop .	39.0	39.05	38.95	38.45	37.80 cm.
Drop fallen .	38.5	38.55	38.40	37.90	36.95 cm.
Alteration .	0.5	0.50	0.55	0.55	0.85 cm.

This bubble was blown from a solution containing 10 per cent. ammonium oleate and 50 per cent. of glycerine.

A bubble of similar size, but resting on a ring, varied in vertical diameter as follows:—

42.6 cm. when fairly thick, at first.
 43.5 „ 15th day.
 43.0 „ 16th day, orange to amber.
 43.3 „ 17th day, 80 per cent. black.
 43.0 „ 18th day, four-fifths deep orange, one-fifth purple ;
 thus rising higher on its ring-support as it became thinner.

The maximum amount of distortion by loading which a bubble of this size can maintain was observed in one case by expanding the bubble until the distortion at the rim-support, 4 cm. in diameter, showed that it was nearly being dragged off. The dimensions were then 45.4 cm. vertically and 40.1 cm. horizontally (ellipticity 11.7 per cent). The diminution in vertical diameter by the release of a single drop was 2.1 cm., showing the near approach to instability. After fourteen days the drainage reduced the loading of the bubble so that the vertical diameter became substantially constant, as shown by the following records:—

Day .	.	7th.	14th.	21st.
Diameter .	.	44.3	41.6	41.8

After this date the bubble remained coloured in the lower three-fourths of its area. In this condition the distortion caused by one drop was approximately 1 cm. The persistence of the coloured stage could be maintained by a very minute continuous leak of solution from the reservoir into the supporting nozzle. When the soap

solution supply was stopped the development continued to the black state. When completely black the whole mass, in a bubble 40 cm. in diameter, is of the order of 50 mgms., so that the bubbles are very susceptible to disturbance from shock to the containing vessel. Local or sudden changes of temperature must also be avoided, as strong convection currents are thereby set up. Such currents become evident by innumerable silvery discs (see p. 19) streaming continuously in many directions over the black film. The thicker silvery discs floating for a time on the thinner black film represent excess of liquid drawn in either from the drop below or the ring of liquid, at the contact of the bubble with the supporting nozzle. By the use of closed vessels the nozzle is kept constantly moist, and this is probably a factor in the preservation of black bubbles.

DURATION OF LIFE OF VARIOUS BUBBLES.

The records of a large number of bubbles, up to 46 cm. in diameter, have been preserved. Some extracts are condensed in the following summary :—

TABLE 1.—LIVES OF VARIOUS BUBBLES.*

Three, 16–18 cm., 50 per cent. glycerine, 5 per cent. soap, } water in vessel; temp. 10°–20° C.	28–42 days.
One, 14 cm., 50 per cent. glycerine, 1½ per cent. soap, } water in vessel; half black at end; temp. 4°–11° C.	98 "
One, 20 cm., 50 per cent. glycerine, 5 per cent. soap; } temp. 9–11° C.; over 60 per cent. black at end	95 "
One, 12 cm., 30 per cent. glycerine, 3 per cent. soap; } temp. 10°–20° C.	30 "
Black horizontal film, 20 cm. diam., 50 per cent. glycerine, } 5 per cent. soap; temp. 4°–20° C.	over 1 year.

TABLE 2.—LIFE OF SUCCESSIVE BUBBLES. 40 cm. Bubbles on Ring.

1st 200-litre vessel.	2nd 200-litre vessel.
1st bubble (vessel dry) . . . 3 days	1st, 5 days
2nd bubble (water in vessel) 7 "	2nd, few hours (ring rusty)
3rd bubble (water in vessel) 10 "	3rd, 8 days
4th bubble (water in vessel) 24 "	4th, 18 days
5th bubble (water in vessel, vibration) . . . 19 "	5th, 11 days (hot weather, &c.)
6th bubble (water in vessel) 55 "	6th, 63 days (hanging on ¼ cm. support)
7th bubble (water in vessel, out in yard, frosty at end) 31 "	7th, 42 days (globe became contaminated)

* A hanging bubble kept in air saturated with water vapour, of an initial capacity of 4·5 litres, took 322 days to completely collapse from air transfusion.

The first item of Table 1 includes the first bubble (50 per cent. glycerine, 5 per cent. ammonium oleate), which kept its colour instead of developing to blackness. This was caused by moisture left after cleaning the 5-litre bottle in which it was blown; no more moisture than enough to give a bedewed appearance was left, but this distilled to different parts of the vessel, as the local temperature altered, and resulted in a movement of water vapour sufficient to keep the absorbent bubble thick enough to show colours.

Sharply marked zones of different colours are a feature of such bubbles. For this an undisturbed atmosphere is necessary; otherwise convection currents in the bubble will, by continual mixing, prevent the quiet development of separate colour zones. The temperature alterations must, therefore, be small. From the records of one bubble the following appearances were noted:—

On the 15th day. 20 cm. in diameter: sharp boundary line at "60° N. Lat." between steel-blue above and greenish-yellow below: similar boundary between blue-green and blue-purple at "50° S. Lat." Large drop on bubble.

On the 18th day. Diameter, 19.4 cm.: three sharp line boundaries: green to purple at "30° N.": dark green to light green at "70° S.": light green to thin magenta at "80° S.": intense green disc at lowest part. Drop fallen off.

On the 24th day. Main area of bubble fairly uniform red purple: boundary at "75° N." to pale green above, and to deep green below at "60° S." Graded Newton's rings of mauve and green below this.

The life of the bubble shown in the second item of Table 1 was double that of those in the first item, namely, 98 days instead of about 40 days. The solution used had 10 per cent. of ammonium oleate instead of 5 per cent. as before. This factor, however, had less influence than the generally lower temperature of under 11° C. instead of up to 20° C. as before. Between the 75th and 95th days there was a contraction from 11.4 cm. diameter to 10.4 cm., while still remaining coloured. By the 95th day the bubble had become too dilute to maintain any colour, and accordingly developed to the thinnest or "black" stage in the upper half. On the night of the 98th day the temperature of the Laboratory fell to near freezing point, and the bubble did not survive this change.

The next item refers to a bubble of 5 per cent. potassium oleate in 50 per cent. glycerine. The 12-litre aspirator in which it was blown was well dried, and, further, was placed in a vault where only slow and small temperature variation occurs. In three months the variation was from 9° C. to 11° C. This solution was chosen, because of its property of giving extremely slow development to the "black" stage. The result was that in 95 days the zone of black had only extended down to "25° S. Lat.," the remainder being so thick as only to be feebly coloured with faint pink-and-green rings, probably

up to a hundred times the thickness of the black supporting zone above. The final collapse may have been associated with this condition ; moreover, the potash soap is very sensitive to slight alkalinity of the glass,—no other disturbing cause was observed.

Table 2 shows the lives of two sets of large bubbles under similar conditions, in two vessels of 200-litre capacity (Fig. 4). These vessels were cylindrical glass globes, used in the Laboratory twenty-five years ago in the production of liquid ethylene. They had short necks,

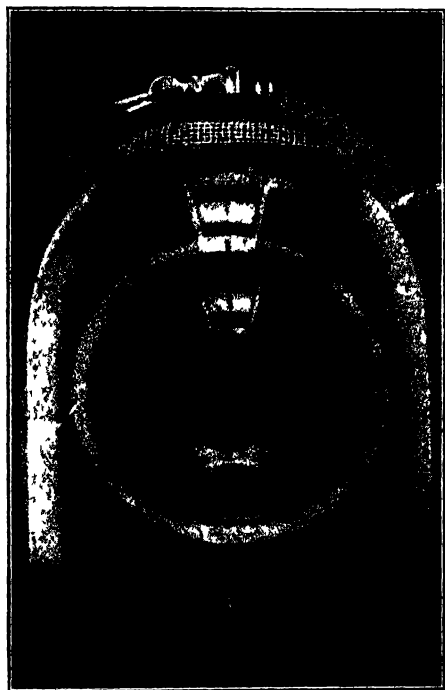


FIG. 4

14 cm. diameter, which were fitted with good, cleansed india-rubber corks to carry the blowing tubes, vent tubes, etc. An oxidised steel wire ring was used to support the majority of the bubbles. These rings were about 12 cm. diameter, and were raised, by three supports of the same oxidised wire, to about 25 cm. above the bottom of the globe. For bubbles so supported the blowing tube was less than 1 cm. diameter ; it had a constriction of about 1 mm. bore, a few centimetres above the lower end. A few drops of liquid from the reservoir above were decanted down to fill the constriction for the

purpose of starting the bubble. The reservoir is shut off by a stop-cock from the blowing tube, as it is not advantageous for the soap solution to be exposed to the current of air used in expanding the bubble; a side tube is sealed in for the air inlet. The blowing tube is mounted, so that it can slide up and down while remaining airtight. A few small bubbles are first blown and run round the supporting ring to wet it. A bubble is then blown to about 4 cm. greater diameter than the ring, while resting on one side of it. This is done by holding the end of the blowing tube sufficiently out of the centre, and steadily raising it until the bubble is about 15 cm. diameter, when it is allowed to come into full contact with the whole ring, and the expansion is continued until the requisite diameter of about 40 cm. is reached. Meanwhile, the blowing tube is continually raised through its sliding support tube in the india-rubber cork, and finally withdrawn by a to-and-fro spiral movement upwards. In one case when the bubble became free from the tube, a complex up-and-down oscillation took place in a period of about two seconds, and with an initial amplitude approaching 3 cm. at the upper periphery. By leaving the blowing tube in the bubble the advantage of an added steady support is secured; this is unsatisfactory when measures of contraction are being made, but it certainly helps to prevent undue disturbance, especially in the early stages, when the bubble is liable to be thick and somewhat top-heavy on the 10 cm. ring.

It can be seen from Table 2 that there is a general increase in length of life of the successive bubbles in both the first and second vessels. The last items, in both cases, show a shorter life; this, however, was due in one case to the vessel being in the open air in winter, whereby its temperature at the end went below freezing point; and in the second case, to the globe becoming contaminated, from the displacement of a badly-fitting tube. The irregularity between the fourth and fifth items was explained by the hot weather (temperature over 20° C.).

The maintenance of colour in such large bubbles was not easy. For this purpose a good circulation of water vapour in the vessel seems desirable, as the mere presence of a litre or two of water in it was not entirely effective. A wet cloth placed on the upper part of the vessel (seen in Fig. 4) by its own evaporation maintained a slightly cooler area, thus promoting the condensation there of drops of water. A flow of water vapour up through the vessel was thus obtained, which being partly absorbed by the glycerine in the bubble did for a time maintain, and even increase, its thickness and colour. In the later stages also, when the bubble material has thus become altered in the relative proportions of its constituents, vaporisation from the bubble may take place, and then the opposite effect is observed; distillation causing the thickness to decrease, so that two or three colours are passed through in as many hours. A few degrees rise of room temperature causes the same change, especially in diluted

bubbles. The lowering of the temperature will then reverse the effect and the bubble is seen to thicken. The ordinary variations from night to day are sufficient to cause many such repetitions in the same bubble. Thus, when it was thought to increase the proportion of water vapour by warming the water in the vessel, and thereby increasing the thickness by a greater absorption, the rise of temperature counteracted any increased absorption; and once more the bubble became thinner. The removal of the wet cloth allows the condensed water to distil off more vapour, which is often sufficient to thicken the bubble. This is best seen when a good condensed deposit is accumulated before blowing the bubble, as was done in one case (see fifth bubble, first vessel) by the application of bags of ice. The bubble, which was then blown, remained almost entirely coloured throughout its life. A small zone of black came and went, and the thickness was reduced once or twice by a damp cloth. The weather was rather warm at first, but became more temperate (the time was August). Finally, the bubble was very much thickened, and probably burst from this cause; for as the bubble became thick, it overhung the ring unsymmetrically, and most probably became lopsided enough to swing round and touch the vessel. The supporting ring was seen to be slightly out of the horizontal, and in vibration due to the working machinery in the room below.

The fourth bubble in the second vessel: during the first week untouched; maintained green and pink colour; thick and overhanging the ring; then frequently treated by damp cloth above, thinned while cloth was on and thickened when cloth was removed; at third operation, bubble half black; next time, the water below was warmed by the arc lamp beam: result, 85 per cent. black obtained.

The fifth bubble in the second vessel lasted eleven days only; short life in the hot weather; disturbed at the end by damp cloth, also by vibration; thinned to silver and black; first three days thickened rapidly by absorption from the deposit of water; immediately after being blown sagged over ring; then steadily thinned through several beautiful grades, until on the fifth day at $19\frac{1}{2}^{\circ}\text{C}$. it was amber and purple, with silver above. Damp cloth then put on; the silver extended all over, followed by a fairly uniform development of black. Two grades of black were noted—the deepest black being only a zone of a few centimetres at the top. The top of the bubble was approximately 1 cm. higher when black than when thick and heavy.

The sixth bubble in the first vessel went quickly black in two days (possibly from an unusual excess of ammonia in the soap solution), and remained so until the end of the first week. It then thickened to various colours for four weeks, and once again went quickly black. This condition remained for three weeks, during which time a steady diminution of diameter was measured. The blowing-tube having been left attached to the bubble, the contraction had by this time narrowed

down the upper part of the bubble till it became a neck. When this divided, the disturbance was probably more than the very dilute and very thin film could survive, for the next morning it had gone.

The seventh bubble in the second vessel was suspended from a 4-cm. nozzle; it lasted from 27th October to 9th December. The temperature fell from 15° C. at first to below 10° C. after the first week. The bubble burst after a sudden rise of temperature from 6° to over 9°, accompanied by a considerable fluctuating fall in the barometer, when it was found, by the optical test, that the air in the globe had become contaminated. This bubble afforded an opportunity for observing the rate of fall of condensation drops. Excluding the preliminary drainage, the results are shown in the annexed diagram (Fig. 5).

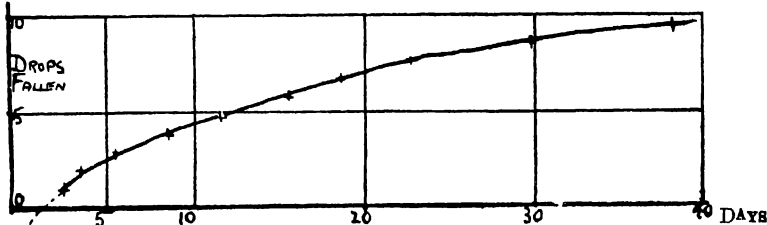


FIG. 5.—ABSORPTION OF WATER VAPOUR BY A 40 CM. BUBBLE.
Rate of fall of drops.

GAS TRANSFERENCE THROUGH BUBBLES AT ATMOSPHERIC PRESSURE.

Long-lived bubbles regularly diminish in diameter, and most rapidly when thinned to "black." The contained air or other gas is at a somewhat higher pressure than the atmosphere in which the bubble stands, and therefore tends to pass out; with the result that there is a continual diminution in size. With black bubbles up to about 15 cm. the change becomes very evident in about a week. Using a cathetometer, the contraction can be observed accurately from day to day. The subjoined diagram (Fig. 6) shows the contraction, measured every third day, of a black bubble in hydrogen. From an initial diameter of approximately 11 cm., by the twenty-third day it had completely contracted. It will be noticed that the rate of contraction was accelerated as the diameter decreased.

The gradational diminution in diameter of black bubbles made from soap solutions of different compositions, and with diameters up to 46 cm., was periodically measured with the cathetometer.

The rate of gas transference from within the bubble outwards at any time can be obtained directly from the mean daily reduction in diameter at that time, and is readily measured by dy/dx , the slope of

the tangent drawn at the desired point of the contraction curve. The amount of the gas transference, in cubic centimetres per day through unit area, is then equal to one half of the daily rate of reduction in diameter, measured in centimetres.

This follows directly from the simple properties of a sphere; for if S and V be respectively the surface and volume, and D the diameter, then $S = \pi D^2$, and $V = \frac{\pi}{6} D^3$, so that $dV = \frac{\pi}{2} D^2 \cdot dD = \frac{1}{2} S \cdot dD$, therefore dV/S , the rate of gas transference per unit surface, $= \frac{1}{2} \cdot dD$, which is half dy/dx , the daily rate of reduction in diameter shown by the slope of the tangent already referred to.

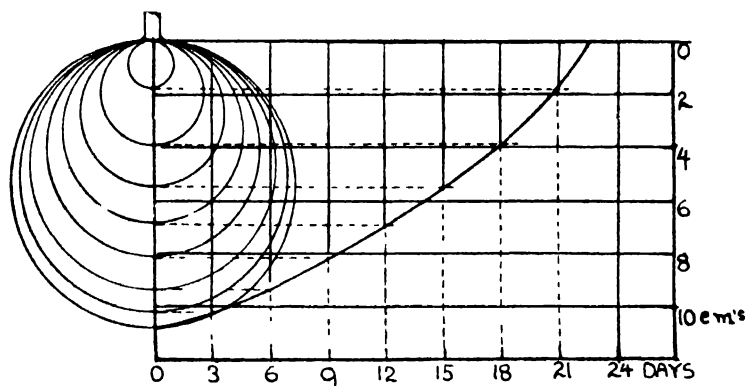


FIG. 6.—BLACK BUBBLE IN HYDROGEN.
Decrease in size at 3-day intervals.

Some of the results obtained are shown in the following Tables 3, 4, 5, and 6, in which are given respectively (1) the diameter of the bubble on which the measures were made; (2) the corresponding internal excess pressure, above the exterior air pressure, given in mm. water; and (3) the measured value of $dD/2$, representing, as shown above, the rate of gas transference in c.c. per day passing out through each square centimetre of the bubble when at the diameter given in line (1).

Gas Transference through Black Air Bubbles.

TABLE 3.—50 per cent. glycerine, $2\frac{1}{2}$ per cent. soap; hanging on glass tube.

Diameter	6	7	8
Internal pressure .	0.30	0.26	0.23
Gas transference rate	0.065	0.035	0.030

TABLE 4.—25 per cent. glycerine, 4 per cent. alcohol, 5 per cent. soap ; hanging on glass tube.

Diameter . . .	10	12
Internal pressure .	0·18	0·15
Rate	0·15	0·11

TABLE 5.—Two large black bubbles (thinned by water condensation) ; hanging on a glass tube.

	(I)	(II)
Diameter . . .	38	38
Internal pressure	0·057	0·057
Rate	0·023	0·015

The corresponding rates calculated for similar bubbles 10 cm. diameter would be : (1) 0·086 ; (2) 0·58 ; whereas a bubble subject to water condensation, but still retaining some colour, contracted from 11 cm. diameter on its 75th day to 10 cm. diameter on the 95th day, being a diminution of 1 cm. in twenty days, giving an average daily rate of gas transference per unit of surface equal to 0·025 cm., or about one-third the calculated rate for a black bubble of the same diameter.

Table 5 may be amplified as follows, to show more completely what is occurring in bubbles of this size :—

TABLE 6.—Gas transference through 38 cm. black bubbles in air (dilute glycerine-oleate solution).

Results		(I) 5 weeks black*	(II) 2 weeks black †
Diminution in diameter . . .	Daily	0·045 cm.	0·03 cm.
	Total	1·58 cm.	0·41 cm.
Diminution in volume . . .	Daily	0·103 litres	0·067 litres
	Total	3·60 litres	0·940 litres
Gas transference through each sq. cm.	Daily	0·023 c.c.	0·015 c.c.
	Total	0·805 c.c.	0·205 c.c.

* No. (I) hanging on a glass tube. † No. (II) less diluted than No. (I), and resting on a steel wire ring.

In the case of a hanging bubble as large as 38 cm., referred to in Table 6, the total reduction in the diameter amounts only to 1.58 cm. in five weeks. The volume of such a bubble is over 30 litres, and the surface has an area of 5,000 square cm., while the total weight is only about half a gram. Being thinned to the "black" stage, it has a maximum thickness of approximately fifteen $\mu\mu$'s; that is to say, one and two-third million such films if superposed would have a total thickness of one inch. The internal excess pressure is of the order of a twentieth of a millimetre of water,

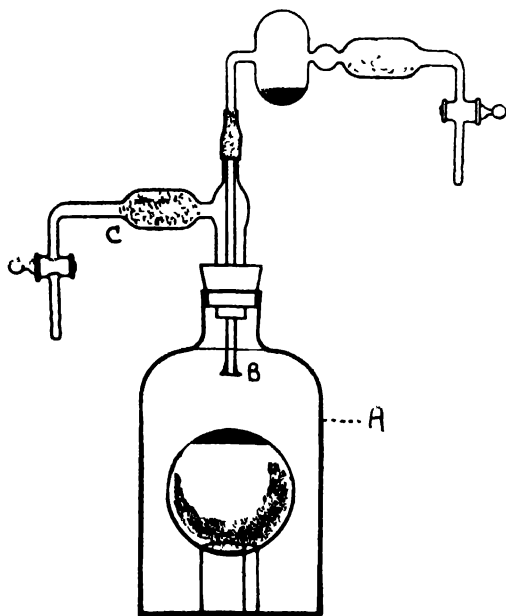


FIG. 7.

or about one fifteen-thousandth part of the pressure of the atmosphere. Nevertheless the actual volume of air which passed out of the black bubble in five weeks was 3.6 litres, or every minute a layer of air molecules some ten to eleven times the thickness of the wall of a black bubble of 38 cm. diameter passed through it. Hence the thickness of the layer of air which at ordinary temperature passes through the film in one second is 10/60ths of the thickness of the film, or 2.5 $\mu\mu$'s—in other words, a layer of air as thick as the film would take six seconds to pass through it. Again, the mean free path in air is 100 $\mu\mu$'s, which is nearly seven times the thickness of the film, and therefore some forty times the thickness of the layer of air passing through the film in one second. Theoretically the internal pressure

in a black bubble of less than about 1 cm. diameter would be sufficient to cause the transference of a layer of gas of a thickness equal to the length of the mean free path. The rate of transference in bubble III. is only about three-quarters of that in bubble I.

A black spherical air bubble about 42 cm. diameter, supported by a nozzle above and a small fixed horizontal glass ring below : thus keeping its vertical diameter constant, altered to an ovoid shape, 33 cm. horizontal diameter, in 109 days. The lessened internal air pressure caused by the ovoid form reduced the rate of the air transference to about one quarter that in bubble I. (Table 6).

Gas Transference through Black Bubbles in Hydrogen.

A few hydrogen bubbles blown in hydrogen were also observed. A suitable vessel for these bubbles is shown in Fig. 7. An oxidised iron-wire ring is seen supporting a bubble, not yet completely black, within the flat-bottomed vessel A (about 3 litres capacity). The filling of the vessel A with hydrogen is attended with considerable difficulty, and requires great care in order to obtain "optical emptiness" in the vessel. The nozzle B should be pushed down nearly to the bottom, while the vessel A is being filled with hydrogen by the tube C (used later as an outlet when expanding the bubble). No Tyndall cone will be visible if the vessel is properly filled. The bubble is then blown on B in the usual way, and expanded and let down to rest on the wetted ring already prepared for it; or it may be left suspended from the nozzle. Both inlet and outlet tubes are protected by glycerined cotton-wool filters.

The contractions observed in hydrogen bulbs were generally more rapid than those of similar-sized air-bubbles, as shown in Tables 7, 8, 9, where the units are the same as in the last Tables.

TABLE 7.—50 per cent glycerine, 5 per cent soap

	Hanging from glass nozzle				Standing on iron-wire ring		
Diameter	4	6	8	10	6	8	10
Internal pressure	0.45	0.30	0.23	0.18	0.30	0.23	0.18
Rate of gas transference	0.22	0.14	0.10	0.058	0.253	0.218	0.190

TABLE 8.—83 per cent. glycerine, 3 per cent. soap, hanging from glass nozzles

Diameter	4	6	8	10
Internal pressure	0.45	0.30	0.23	0.18
Rate of gas transference	0.31	0.25	0.20	0.17

TABLE 9.—Approximately 1 per cent. glycerine-soap ; pale golden colour ; hanging from glass nozzles.

Diameter	4	6	8
Internal pressure	0.55	0.36	0.28
Rate of gas transference	0.285	0.108	0.050

The internal pressure was not determined for every bubble ; the values given above were deduced from results obtained with typical bubbles connected to an alcohol nearly-horizontal displacement manometer. The instrument gave with 1 mm. of water pressure a displacement of the order of 100 mm. of the alcohol column.

A study of these results shows at once that there are obscure factors in some cases, causing notable divergences, even when the conditions are not greatly altered. Other experiments have shown that small differences in composition have in many cases a large effect on the behaviour of these thin films. Table 4 (air bubbles) shows that 4 per cent. of alcohol added to the soap solution increases the rate of gas transference through an air bubble.

The constancy in thickness of the "black stage" is undoubtedly subject to variation in different solutions. Johannott, using a large number of small black films in a Michelson interferometer, found that there were at least two values for the thickness of the black film he measured, and that the additions of either glycerine or potassium nitrate tended to give the thicker of the two.* In last year's Discourse a description of five distinct grades of black was given, obtained with soap solution containing over 30 per cent. of glycerine. The film covered a thin glass frame in an exhausted glass vessel. These grades were seen to be unstable, coalescing to the deepest or thinnest black when a portion of soap solution was brought in contact with the lower part of the glass frame. It is possible that a few per cent. of alcohol, with its low viscosity and surface tension, might result in a still thinner black stage.

GAS TRANSFERENCE THROUGH BUBBLES AT PRESSURES OTHER THAN ATMOSPHERIC.

A bubble of about 10 cm. diameter, shown in an exhausted flask (Fig. 2), in which the air pressure had been reduced to the order of a fraction of a mm., was seen to contract visibly from the rapid percolation of the air from within outwards. Under such con-

* "Thickness of the Black Spot in Liquid Films." By Edwin S. Johannott, Jun., Ryerson Physical Laboratory, University of Chicago. Phil. Mag., xlvii., p. 501.

ditions the small internal excess pressure of about 0.2 mm. water, necessary to maintain a 10 cm. bubble, is a very large proportion, say about 10 per cent., of the total air pressure in the flask. There is, therefore, a proportionately small resistance to its percolation through a film sufficiently thin. As the air pressure in the vessel is increased, the time for complete contraction becomes greater, because the internal excess pressure is a relatively smaller proportion of the total opposing pressure; thus when the containing vessel is at atmospheric pressure, the 10 cm. bubble is distended by only $\frac{1}{100}$ th of this total pressure. There is therefore a proportionately small force urging the contained air to pass out compared with that where the vessel was under a pressure of only a fraction of a mm. The result is naturally that the complete contraction takes weeks instead of minutes. In the same way if a bubble be formed in a strong glass vessel charged to, say, 10 atmospheres, then even after six months, during the major part of the time being black, no sensible diminution in diameter was detected.

The measures of contraction at very low pressures were hindered by the difficulty in securing uniformity of thickness in the film. The black bubbles when obtained are extremely fugitive, as they contract so quickly. Then also the ammonium oleate solutions, which are so well adapted for obtaining black bubbles, do not remain of the same composition under low air pressures, due to the removal of the volatile easily-dissociated ammonia.

The results of some of the attempts with ammonium oleates are given in Fig. 8, showing the contraction at pressures of 1 mm. and 5 mm. Hg. respectively, with approximately the same bubble thickness. The curves in Fig. 9 show the relative rates of contraction with potassium oleate at three different thicknesses of bubble, all at the same pressure of just over 1 mm. Hg.

The first of these two diagrams shows that at less than 1 mm. pressure of air in the vessel, a 14 cm. bubble composed of 3 per cent. ammonium oleate in 30 per cent. glycerine, of intense green coloration, contracts completely in about 17 minutes; whereas if the air pressure be raised to 5 mm., the contraction of a similar bubble has only gone from 14 cm. to $11\frac{1}{2}$ cm. in the same time, and to 10 cm. in 25 minutes. The second diagram shows that a bubble 10 cm. in diameter, composed of 5 per cent. potassium oleate, 50 per cent. glycerine, and almost too thick to show colour, takes 47 hours to contract to 6 cm.; but when a bubble of similar size and composition is thinned to intense green, the same amount of contraction occurs in 9 hours; when further, the black stage is secured, the time for complete collapse from 3 cm. diameter is only 25 minutes. The green bubble, from its graph, would have taken from 2 to 3 hours for the same contraction. Such preliminary results may serve at least to point the way to a more complete inquiry.

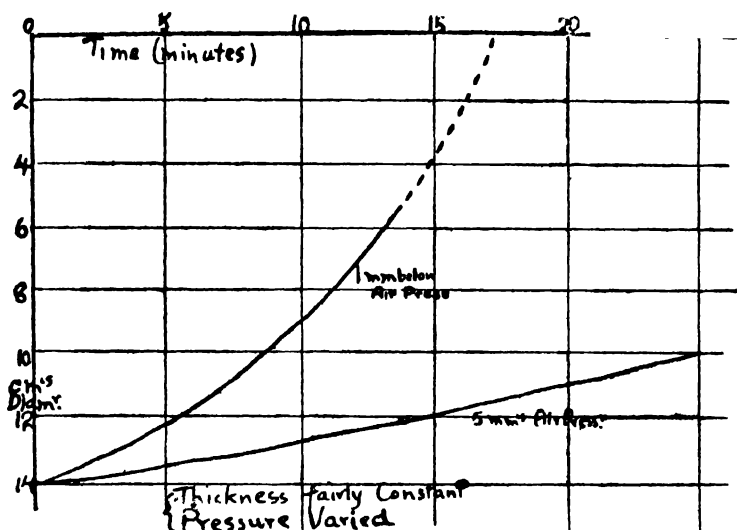


FIG. 8 BUBBLES OF AMMONIUM OLEATE, 3 PER CENT. IN 30 PER CENT GLYCERINE Thinned to first green.

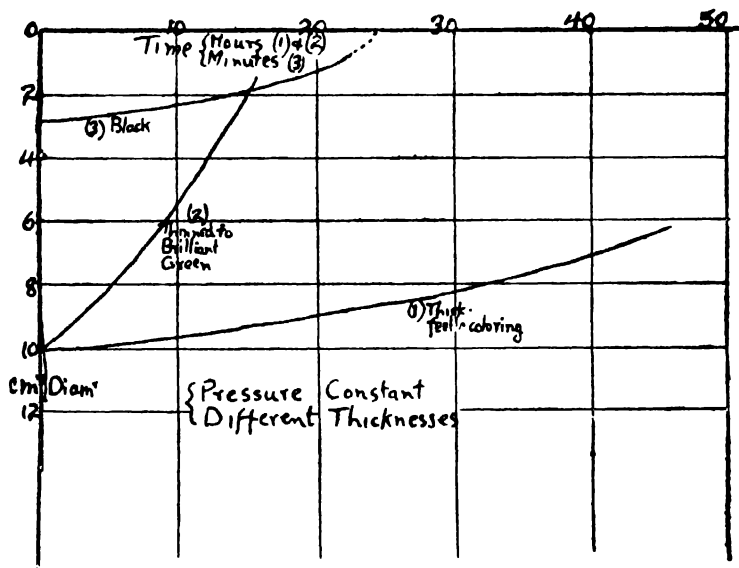


FIG. 9.—BUBBLES OF POTASSIUM OLEATE, 5 PER CENT IN 50 PER CENT GLYCERINE. Air pressure over 1 mm. Hg.

EFFECT ON THE GAS TRANSFERENCE RATE OF THE COMPOSITION OF THE SOAP SOLUTION.

The internal excess pressure P , in a bubble of constant composition, and therefore of constant surface tension T , enclosed in a vessel sealed off from the atmosphere, varies inversely as the diameter D , according to the law $P = 4T/D$.

Hence if the rate of gas transference varies directly as the internal excess pressure, it will consequently vary inversely as the diameter. Now, in Fig. 6, taking the origin at the point where the bubble vanishes, and measuring x (time) horizontally to the right in days, and y (diameter) vertically downwards in cms, we found that the gas transference was measured at any time x by $-\frac{dy}{dx}$; hence $-\frac{dy}{dx} = \frac{k}{y}$.

where k is a constant, the graph of $\frac{dy}{dx}$ to $\frac{1}{y}$ is a straight line, and the curve of contraction is the parabola $y^2 = D_0^2 - kx$, where D_0 is

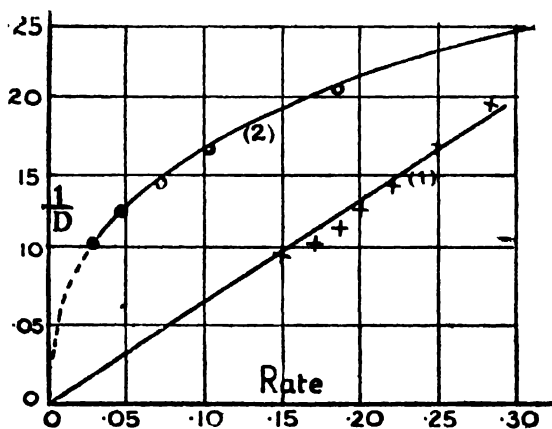


FIG. 10.—GAS TRANSFERENCE THROUGH BUBBLES

Rates plotted with reciprocals of diameters (1) Black H bubble of constant composition (2) Golden H bubble of increasing dilution

the initial diameter—a result usually found to be the case. The equation of the particular curve in Fig. 6 is $y^2 = 121 - \frac{121}{28}x$.

But, when a bubble partly composed of glycerine is exposed to water vapour and thereby progressively diluted, then the surface tension will increase; and the internal pressure will rise at a greater rate than would be due to diminution of diameter alone. The graph of the rates of gas transference, plotted with the reciprocals of the corresponding diameters, would no longer be a straight line. The next figure (Fig. 10) shows the graphs obtained in the case of (1) bubble

of constant composition, (2) bubble of glycerine solution subjected to absorption of water vapour. In this second case (see also Table 9) the rate of gas transference $dD/2$ (plotted as abscissæ) is increasing more quickly than the inverse of the corresponding diameters $1/D$ (plotted as ordinates)—a fact which could be explained (1) by an increase in the surface tension, with a resulting proportional increment in the internal pressure of the contracting bubble; and (2) by a more rapid percolation of hydrogen through the diluted film.

It is evident that further comparative experiments are necessary with more dilute films of constant composition before these effects can be differentiated. Preliminary attempts showed that a solution containing only 0.15 per cent. of ammonium oleate with 1.5 per cent. glycerine can give a fairly long-lived bubble (one such in hydrogen contracted completely in 28 days from 8 cm. diameter: see p. 29). But the maintenance of constant thickness is not easy, because with bubbles of such dilution even slight variations of temperature cause recurrent colour changes: it is specially difficult to maintain the black stage.

No great alterations of temperature occurred in any of the above experiments, but distinct evidences of variations from this cause were noted on several occasions. The laws governing this factor have yet to be elucidated.

ALTERATION OF THICKNESS BY CONTRACTION. SILVERY DISCS. CONSTANCY OF BLACK ZONE.

A contracting bubble that remains constant in weight will, of course, become thicker as the surface diminishes. The thickness will vary inversely as the square of the diameter, provided the capillary, viscous, and gravitational forces did not come into play. For small changes, on the simple theory, the rate of logarithmic increase of thickness will be twice the rate of logarithmic diminution of diameter. This is a property of the sphere that may be expressed as follows:—When S = surface, T = thickness, ρ = specific gravity of the liquid composing the bubble, then, since $S = \pi D^2$,

$$\text{Mass} = S T \rho = \pi D^2 T \rho$$

and as the mass and composition are assumed unaltered, this gives

$$D^2 T = \text{constant, or } T \text{ varies as } \frac{1}{D^2} \quad . \quad . \quad (1)$$

i.e. the thickness varies inversely as the square of the diameter, and is true for all magnitudes. Differentiating,

$$2 T D \cdot dD + D^2 \cdot dT = 0, \quad \text{or } \frac{dT}{T} = -2 \frac{dD}{D} \quad . \quad (2)$$

which can be put in the form

$$d(\log T) = -2 d(\log D) \quad . \quad . \quad . \quad (3)$$

Thus the rate of logarithmic increase of the thickness is twice the rate of logarithmic diminution of diameter.

In black bubbles increase of thickness can be observed if the contraction is rapidly effected by opening the closed bubble to the air, or by cautiously removing the air by suction ; but the immediate effect is not to produce a coloured bubble. What happens is that small silvery circular discs (see p. 8) break out over the surface of the black bubble, and these represent the aggregations of liquid resulting from the contraction, for they are much thicker than the black film through which they move. They very soon settle to the lower parts, and there slowly coalesce to a small graded coloured area. This usually contracts in a short time to a much smaller zone, too thick to show colour, and finally very little more is left than a small drop surrounded with a narrow silvery band on the otherwise black bubble. Large black bubbles contracting by gas percolation go too slowly for these effects to be observable, but the final result is the same : a drop of liquid slowly collects on the black bubble, and may in large bubbles grow sufficiently to fall off, after causing a progressive elliptical distortion.

Comparable behaviour is shown when one or two drops of solution per minute are allowed to trickle into a black or partly black bubble. Coloured streaks appear and pass downwards from places all round the supporting nozzle into which the liquid is fed ; later on the streaks break up into coloured discs, falling slowly by sinuous paths and with diverse motions. However, they all pass through the black portion, and after remaining for several minutes as a mass of distinct many-coloured particles, form by coalescence a coloured zone below round the drop. If the liquid is fed in more rapidly, the coloured zone will rise to a certain extent, but, in single bubbles, a large area of black almost always remains. The feeding of the liquid may be cautiously increased almost to a stream ; the bubble is then, of course, much disturbed at the boundary of the black zone, as well as elongated by the loading, and drops fall away in steady succession. The paths through the black zone may then become so thick as to be transparent threads of liquid, without any colour in themselves, but causing coloured rays and patches to flash outwards from their paths.

It was further observed that when a partly coloured bubble quickly altered in size, the black zone remained roughly constant in area, being independent of the extended or contracted surface. The thickness seemed to alter at the expense of the coloured portion, which consequently changed in tint. A bubble is allowed to develop to blackness for about one-third of its surface, the remaining two-thirds grading from a silvery boundary at the black, through golden colour to deep steel-blue. This state is reached in a few hours with a solution composed approximately of 34 per cent. neutral ammonium oleate in 33 per cent. glycerine, with a slight excess of ammonia. Now gradually expand the bubble by a slight reduction of the external pressure. Meanwhile the level of the black boundary as well as the

change of diameter are observed. The coloured area is seen to change from steel-blue to blue-purple through magenta and deep amber until almost the whole of it is a full golden colour as a result of the diminished thickness, which however is still of the order of fifteen times that of the black. During this time the black boundary has risen slightly in level; but when the area of the black zone is calculated at successive stages, the value is found to remain constant to within a few per cent. All liquid must be well drained from the hanging bubble by leaving a drainage tube in contact with the drop position, during the preliminary development to partial blackness. Two sets of observations, showing the approximate constancy of the area of the black zone, while the coloured portion is varying to a large ratio, appear in Table 10 below.

TABLE 10

Whole Bubble		Black Zone	Coloured Zone	Ratio	
Diam (cm)	Area (cm) ²	Area (cm) ²	Area (cm) ²	Coloured	Black
(i) 17.55	967.6	90.4	877.2	9.7	
15.75	779.2	94.5	684.7	7.3	
13.70	589.6	94.7	494.9	5.2	
11.60	422.7	91.1	331.6	3.6	
9.54	286.0	81.7	204.3	2.4	
(ii) 19.1	1146	77.7	1068.3	13.9	
16.1	814	76.4	737.6	9.7	
13.1	539	74.5	464.5	6.2	
10.1	302.5	69.1	233.4	3.4	
7.1	158	35.1	122.9	3.5	

Thus, from the first four observations, the actual black area of the first bubble only varied some 2 per cent. from its mean value 92.7 cm.², while the coloured-to-black ratio fell from 9.7 to 3.6, or some 63 per cent.; similarly the actual black area of the second bubble varied about 5 per cent. from its mean value 74.5 cm.², while the coloured area fell from nearly 14 times to 3½ times the black area—a drop of over 75 per cent.

ABSORPTION OF WATER BY BUBBLES COMPOSED OF OLEATE GLYCERINE SOLUTION.

When boiled water is introduced into a vessel which holds a bubble composed partly of glycerine, water vapour is absorbed and

the normal thinning of the bubble to the black stage is prevented. There is instead an increase in thickness, causing gradational changes of colour : the bubble sags down from the increase in weight ; successive drops accumulate and fall off, at first, maybe, two or three in a day, decreasing rapidly in number as the dilution proceeds, until when the soap-glycerine is reduced to 1 or 2 per cent. the interval between the drops grows into many weeks, and the drainage practically

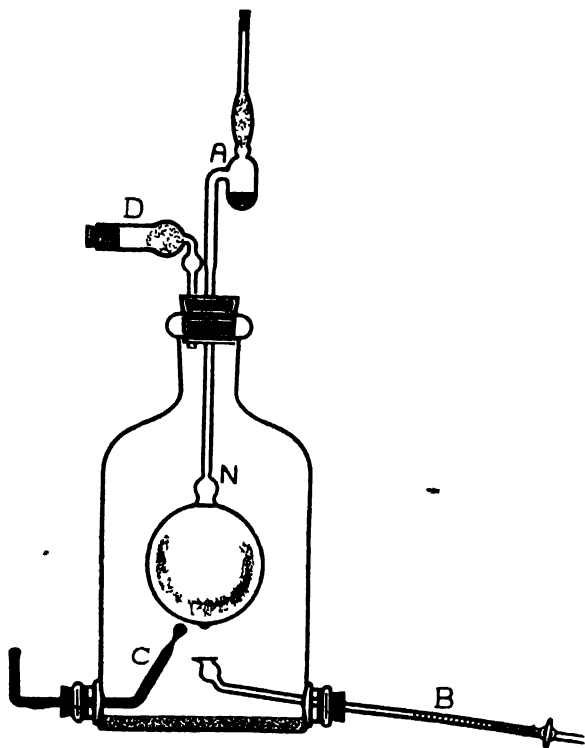


FIG 11

ceases. When very diluted the black stage is finally reached, and may remain, provided the temperature is steady ; but usually much fluctuation of colour takes place, the black even recurring many times.

The washings of several such bubbles were collected in a graduated tube, and periodically weighed and analysed. In the case of a bubble of glycerine and ammonium oleate, the analysis for most purposes consisted simply in heating the liquid—in an oven at 90° – 95° C.—until constant in weight. The contained glycerine and oleic acid

were thus left practically in the same relative proportions as in the original bubble, water and ammonia being driven off. If necessary, the ammonia was separately estimated by Nesslerising. This is one advantage attending the use of ammonium oleate in such bubbles, as compared with the oleates of a non-volatile base like soda or potash.

The arrangements employed are shown in Fig. 11. The blowing-tube A, with its nozzle N to carry the bubble, is supported in an india-rubber cork fitting the neck of a 10 to 12-litre tabulated "aspirator" vessel D is a bulbous vent tube, and is packed uniformly,

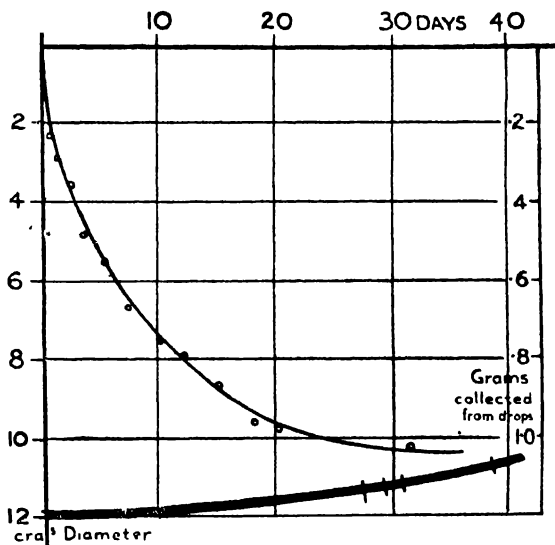


FIG. 12.—AIR BUBBLE OVER WATER REMAINS COLOURED
Contraction and condensation

but not tightly, with cotton-wool moistened by glycerine. This allows any variations of atmospheric pressure to be equalised without endangering the purity of the internal atmosphere. B is the graduated collection tube fitted in the lower tubulation; its nozzle, inside, is directly under the drops which accumulate on the bubble. Before opening the stop-cock on B, to draw off the accumulated liquid, the stopper in D is removed to allow the equalisation of barometric pressure, otherwise the small quantities of liquid could not be smoothly withdrawn; alternatively, D may remain open. Before commencing observations any excess liquid is removed from the bubble by drainage along the rod C. This is also done very effectively by a small bundle of very thin glass rods, about $\frac{1}{4}$ mm.

diameter, tied together by thin aluminium wire ; but the drawn-out glass rod C acts automatically when placed vertically just below the drop, for, as this grows, it descends by its own weight, and, enveloping the rounded end of the rod, drains down along the drawn-out neck, and the lightened bubble rises off the rod.

After the bubble has thus drained for several hours, the boiled distilled water is run in. The collecting tube may be utilised for this by turning down the nozzle and tilting the vessel, or a separate inlet tube with stop-cock may be fitted.

In order to isolate the bubble from the soap solution in A, and prevent any distillation or intrusion of extraneous liquid, the reservoir in some experiments was removable. For this purpose a conical ground joint was made in the tube A above the india-rubber cork.

The contraction of the bubble is somewhat irregular, because of the constantly varying thickness of the film, shown by the beautiful changes and gradings of colour. In the case of an air bubble the contraction is also relatively slow. Thus (Fig. 12) one of 12 cm. diameter only diminished in forty days to 11 cm. A second one, of 21.4 cm. diameter, contracted in five months to 16.6 cm. A third one, of 15.8 cm. diameter, took a little over six months to contract to a plane film on the supporting nozzle. In wet hydrogen, however (Fig. 13), an 11 cm. bubble, -under conditions of somewhat lower temperature, -contracted completely in about three months ; almost all this time, moreover, it was of sufficient thickness to show strong colours.

The form of the contraction curve of the hydrogen bubble is fairly regular (considering the variations of thickness as shown by the colour changes), and of similar form to that given by black bubbles of constant composition. Its collection curve, of similar type, in which the amounts collected by drainage are plotted as ordinates to the time of collection as abscissæ, is also shown in Fig. 13.

Similar contraction and collection curves are shown in Fig. 12 and Fig. 13 for air and hydrogen respectively. The left-hand vertical scales are for cms. in diameter for the contraction curves ; the right-hand scales are for grams of liquid collected for the collection curves. The collection curve appears roughly as an image of the contraction curve, showing that, whereas the contraction is slow at first, increasing parabolically to the final disappearance, the condensation and drainage begins rapidly when the bubble contains concentrated glycerine, and falls off to zero as the dilution asymptotically approaches completion.

Careful measurement of such curves given by both air and hydrogen bubbles revealed them to be parabolic during the initial period before the surface became sensibly reduced by contraction. From this it follows that during this period the rate of collection is inversely as the total amount collected ; just as in the contraction

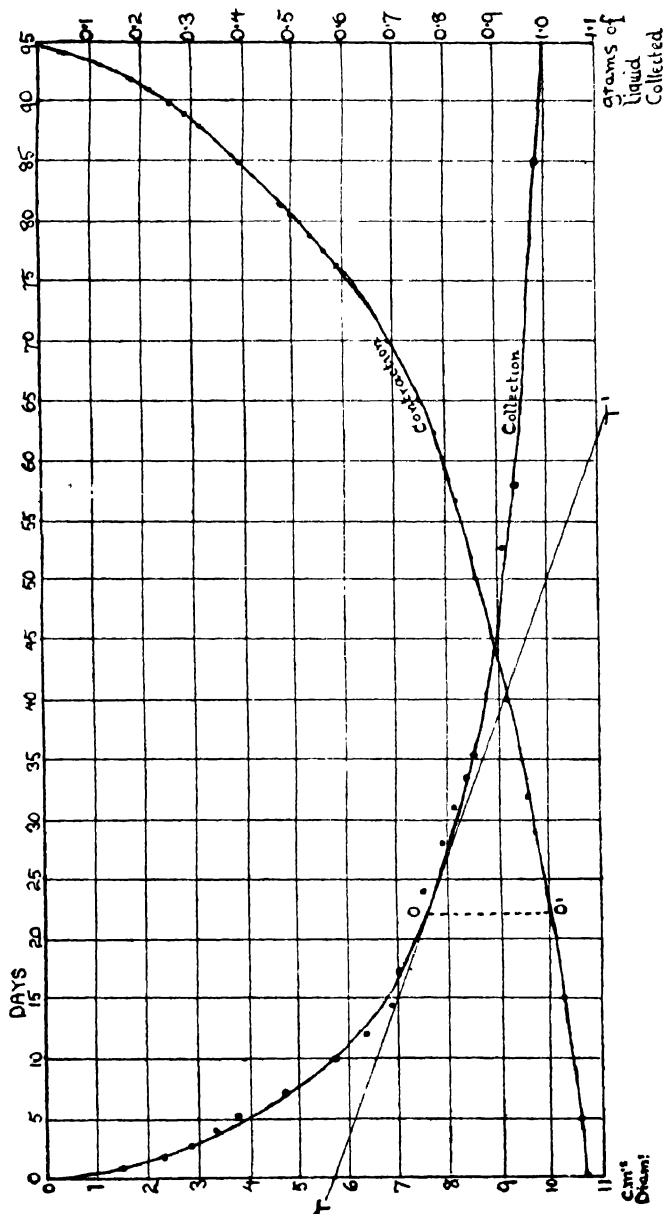


FIG. 13.—HYDROGEN BUBBLE IN HYDROGEN SATURATED WITH WATER VAPOUR. Contraction and water absorption.

curves the rate of diminution of diameter is inversely as the diameter. The equation of this first portion of the drainage curve shown in the above figure for a hydrogen bubble is $y = 0.1787 \sqrt{x}$, where y is in grams, and x is in days.

The approach to agreement between the observed and calculated values thus resulting is seen in the following Table :—

TABLE 11.

x days		1	2	3	4	6	8	10	12	14
y gms	Observed .	0.18	0.26	0.305	0.36	0.45	0.52	0.57	0.62	0.66
	Calculated	0.18	0.25	0.309	0.36	0.44	0.51	0.57	0.62	0.67

In half a day 0.1 gram of liquid had been collected ; in eight days 0.5 gram was obtained ; but a total of 1.0 gram was only reached on the 95th day.

The corresponding expression in terms of mgms. from each sq. cm. of the bubble surface is $y = 0.514 \sqrt{x}$. The result given by the bubble under similar conditions in air instead of hydrogen was $y = 0.554 \sqrt{x}$. (See Fig. 12.)

The final composition of the bubble is thus relatively very little different from water. As a confirmation of this the original bubble solution (5 per cent. of ammonium oleate, in 50 per cent. glycerine) was diluted thirty-three times with carefully prepared-boiled distilled water. A bubble 8 cm. diameter was then blown from this solution. It lasted until completely contracted after exactly four weeks. During most of this time it was coloured amber to purple ; on three or four of the warmer days nearer the end (temperature about 10° C.) it reached a semi-black stage peculiar to these very dilute bubbles. Only one drop accumulated, caused by the shrinking of the bubble. This bubble has already been referred to in connection with gas transference through bubbles of graded dilution (see p. 24).

By investigating the condensation on unit area of the bubble, instead of on the whole bubble, a simple expression can be found that is applicable to the whole of the drainage curve, instead of only to the initial period of constant surface. The rate per unit area is of course found by dividing the weight of total drainage by the mean surface of the bubble over the period measured. This is most readily done by drawing a succession of tangents, TT' , to the collection curve (fig. 13). The slope of these successive tangents along the curve, gives the rates of collection at successive times from the whole bubble surface. The surface each time is obtained from the corresponding diameter, obtained by drawing the ordinates OO' to cut the

contraction curve. By dividing the total daily drainage rate given by the slope of the tangent TT', by the corresponding surface at that time, there results the rate of condensation per unit area. The values thus accruing are set out in the first three horizontal rows of Table 12, with the corresponding day in the fourth row:—

TABLE 12.

Daily rate of condensation	0.049 0.031 0.017 0.008 0.006 0.004 0.003 0.0015									
Surface	353	346.3	333.3	314	2	233.5	254	5	227.0	153.9
Rate per unit area $\times 10^4$	13	9	0.495	0.534	0.282	0.226	0.185	0.137	0.097	
Day	4	8	14	22	33	43	52	70		

By plotting the third and fourth rows as ordinate and abscissa, a new and more fundamental curve is obtained, which is shown in Fig. 14.

An examination of this curve shows that the alteration of the rate of condensation *on unit area of the bubble* after the fourth day is practically hyperbolic as regards time. The expression most nearly fitting the curve is found (by plotting the results logarithmically) to be $xy = 0.705$, where x represents the time in days and y the milligrammes of condensation on each square centimetre. Calculated points are marked "x" on the diagram, and values obtained from observations as above are marked "O."

By bursting bubbles in a weighed vessel, it was found that at the mean thickness which these bubbles maintain under the given conditions (shown by their colour) they have a weight of very approximately 0.1 mgm. per square cm., and are therefore 0.001 mm. thick. Hence, in the equation just given, y may also represent the weight (in milligrammes) condensed per day on each 0.1 mgm. of the bubble. The resulting values calculated for certain days are set out in the following Table 13, together with the corresponding values obtained directly from the tangents to the original contraction curve:—

TABLE 13.

$x = \text{days}$	1	2	4	8	10	14	22	38	43	52	70
$y = \text{mgms. of condensation per mgm. of bubble}$	Calculated 0.705 0.352 0.176 0.090 0.071 0.050 0.032 0.021 0.016 0.014 0.010 Observed . — — 0.130 0.088 — 0.053 0.028 0.023 0.019 0.014 0.010										

The calculated values are at first too high, but later vary slightly on either side of those directly deduced from observations (see Fig. 14).

The values in milligrammes per day, of the rate of absorption

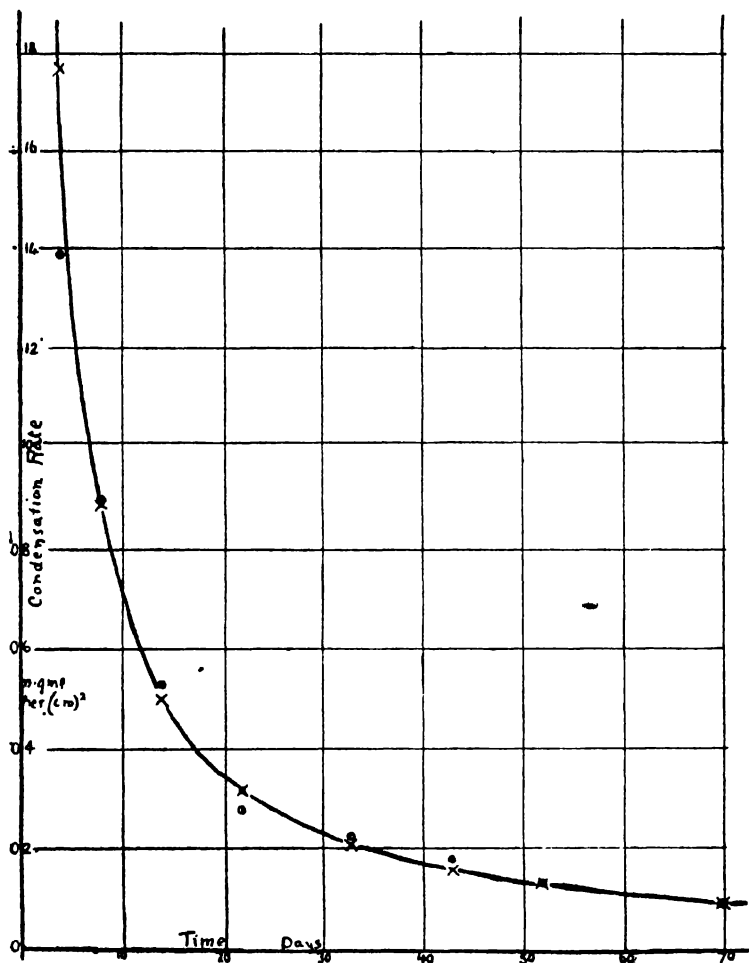


FIG. 14.—CONDENSATION ON BUBBLE IN WET HYDROGEN.
Rate of condensation, plotted to time.

on unit area with an air bubble $15\frac{1}{2}$ cm. in diameter, are given in the subjoined Table 14. They were deduced from the weights of liquid collected in the periods named. The composition of the

bubble was 50 per cent. of glycerine with 5 per cent. of ammonium oleate. This shows the rapid reduction in the daily rate of con-

TABLE 14.

Period	Ratio of Water-vapour Absorption
1st day	0.452
2-9 "	0.073
10-21 "	0.014
22-34 "	0.003

densation occurring within a month, -namely, from 0.452 mgm. at the beginning down to 0.003 mgm. at the end.

ALTERING COMPOSITION OF THE BUBBLE DRAINAGE.

The variation of the composition of the liquid draining from the bubble, during the early portion of these experiments, is shown in the next two diagrams.

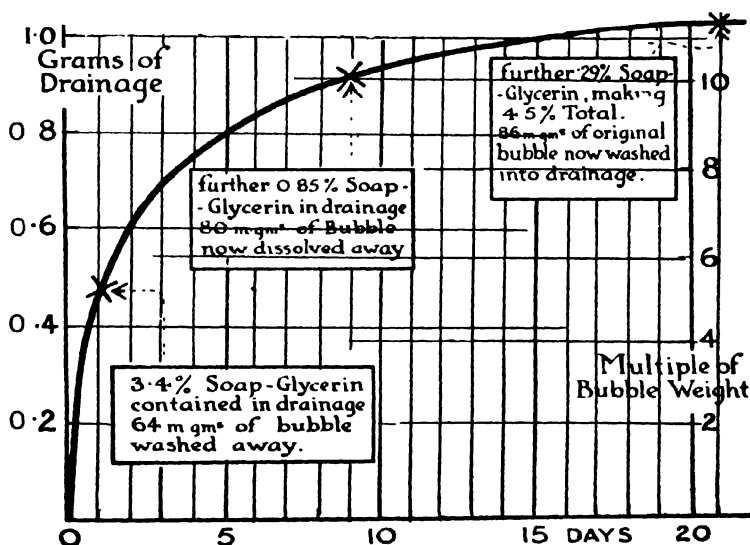


FIG. 15.—ALTERING COMPOSITION OF LIQUID COLLECTED FROM BUBBLE WHEN DILUTED BY CONDENSATION OF WATER. 16 cm. air bubble; 55 per cent. soap-glycerine.

Fig. 15 shows the parabolic increase in the weight of the "drainage," with time; on a separate scale of ordinates, on the right-hand side, is marked the multiple of the original bubble weight equal to the amount of liquid collected. The three points marked are:—

- (1) 0.5 grm. of liquid in 1 day; being over 5 "bubble weights."
- (2) 0.9 " " 9 days; " 10 " "
- (3) 1.0 " " 21 " " 11 " "

At each of these points the composition of the drainage, as well

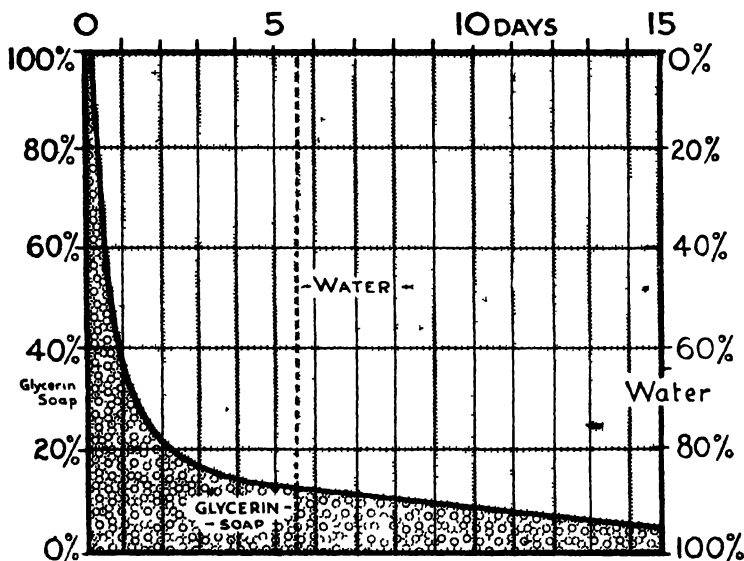


FIG 16 ALTERING COMPOSITION OF BUBBLE WHEN DILUTED BY CONDENSATION OF WATER 16 cm air bubble

as the actual weight of the bubble which had then been washed away, were as follows:—

- (1) 3.4 per cent soap-glycerine; 64 mgms of original bubble washed away.
- (2) Further 0.85 per cent. soap glycerine; 80 mgms. of original bubble now washed away.
- (3) Further 0.29 per cent. soap-glycerine; 86 mgms. of original bubble now washed away.

In Fig. 16 the ordinates on the left show the decreasing percentage of soap-glycerine in the bubble, and on the right the consequent increase in the percentage of water, as the experiment proceeded. The

number of days elapsing are again marked as abscissæ. The dotted ordinate shows, for example, that the bubble on the fifth day had nearly 90 per cent. of the original soap-glycerine replaced by water, and consequently only 10 per cent. of the soap-glycerine which was present in the original solution then remained; this was reduced on the fifteenth day to only about 3 per cent., but afterwards the rate of dilution was much less.

This intrinsic dilution curve agrees in form with that in Fig. 14, which shows the deduced rates of condensation per unit mass (0.1 mgrn.) of the bubble with time. The one result follows from chemical measures of the alteration of drainage composition, while the other follows from the combined periodical observations of the weight of drainage and the contraction of the bubble.

The second part of this investigation dealing with Bubble-Complexes I hope to detail in a future Discourse.

W. J. Green, Esq., B.Sc., and J. W. Heath, Esq., F.C.S., Assistants of the Royal Institution, have aided in the course of the enquiry.

[J. D.]

Friday, March 30, 1917.

COLONEL EDMOND H. HILLS, C.M.G. R.E. D.Sc. F.R.S.,
Secretary and Vice-President, in the Chair.

J. H. JEANS, M.A. F.R.S.

Recent Developments of Molecular Physics.

As the subject of my discourse this evening I propose to take the surprising developments in the fundamental conceptions of physics which have been forced upon us in the last few years. In the closing year of last century, Lord Kelvin delivered a Friday evening discourse, taking as his title "Nineteenth Century Clouds over the Dynamical Theory of Light and Heat." He said: "The beauty and clearness of the dynamical theory which asserts light and heat to be two modes of motion is at present obscured by two clouds." The cloud over the dynamical theory of light centred round the question of the motion of the earth through the ether; that over the dynamical theory of heat was concentrated about the famous theorem of Equipartition of Energy. In the seventeen years which have elapsed since then, the attempt to remove these clouds has led to the introduction of two new principles—or perhaps it is better to speak of them as theories, since they are both still in a tentative stage. The Theory of Relativity has been introduced to remove the first cloud, and the Theory of Quanta to remove the second.

These are, perhaps, the two most revolutionary theories that have been seriously considered by science for some centuries. They are revolutionary especially because they involve a new philosophical and metaphysical outlook which implies a complete break from that formerly held. It need hardly be said that the new theories are still very far from having achieved universal acceptance, but whether they ultimately prove to be true or not, the mere consideration of them has beyond dispute done a great deal towards suggesting a way out of the *impasse* in which molecular physics found itself at the end of last century. The two clouds of which Lord Kelvin spoke are not yet completely dissolved, but rays of light are appearing here and there, and the vista beyond, interpret it in any way we will, is certainly one of the most interesting and fascinating that has ever spread itself before the physicist.

Let us begin with a very brief consideration of the first cloud. The astronomical phenomenon of the aberration of light is known to all. To catch the light from a given star, the astronomer must not point his telescope towards the position of the star, but in a direction obtained by compounding the velocity of light with the velocity of the earth in space. The principle is substantially the same as that on which, when rowing through a strong current, the nose of the boat must be pointed up-stream above the spot it is desired to reach. If light is brought to us in the form of ether waves, the phenomenon of aberration shows that the earth must be moving through a stagnant ether, so that to us on the earth there must appear to be a current of ether streaming past the earth.

It is natural to attempt to measure the velocity of this stream, and so determine the earth's absolute velocity in space. In the famous Michelson-Morley experiment, which was designed to this end, a beam of light was split into two parts. One part is sent up the ether stream and comes down again to the starting point after reflection by a mirror, while the other half is sent an equal distance across stream, and again comes back after reflection. Thus the total length of path is the same in each case, and if the earth were at rest in the ether, the time occupied in going and returning would be the same for each ray. But if there is a stream of ether moving past the earth, it is readily seen that the second half of the beam must gain in time on the first, for the time lost in moving against stream by the first ray is not fully compensated by the gain in time when moving with the stream. The experiment was arranged so that any difference in the time of the two rays would show itself in the formation of interference fringes, and this difference would give a measure of the earth's velocity through the ether. But the experiment, repeated with all possible checks and refinements, refused to disclose any motion of the earth through the ether at all, and other quite different experiments designed to the same end gave one and all precisely the same reply.

Thus, assuming that light consisted of waves in the ether, experiment and observation led to the conclusion that the ether must be at rest, and the earth at rest in the ether, so that the evidence seemed, if strictly interpreted, to lead back to the geocentric universe of pre-Copernican days. This was the cloud over the dynamical theory of light.

From the attempts of Lorentz and Einstein to unravel this contradiction, the theory of relativity has arisen. It says in effect: "The existence of an ether is conjectural, while the results of the Michelson-Morley and other experiments are certain. Let us abandon the dynamical interpretation of light, which is based on the conjectural existence of an ether, and examine what laws are obtained by starting from the hypothesis that all attempts to measure the absolute velocity of the earth, or of any other mass, must necessarily

lead to a *null* result." On this basis, supplemented by certain extensions and generalisations, it is found possible to construct a definite and consistent system of laws. They of course differ from the dynamical laws based upon the supposed existence of an ether, but they differ only where relative motion is involved, because the relativity theory makes its laws agree with those of ordinary dynamics when there is no relative motion. Wherever the old and the new theories differ, an appeal to experiment has so far invariably decided in favour of the new theory of relativity. The most recent triumph of the new theory is of such great interest that it may perhaps be mentioned in some detail.

Gravitation has always stood aloof from other physical phenomena. Since Newton formulated the law of the inverse square of the distance, nothing has been added to the law and nothing taken away. Except that it represents a natural weakening of gravitational effect by spreading out in space, no explanation of the law has ever been given, nor even a plausible conjecture as to the relation between gravitation and other physical agencies. Recently Einstein has found that the Newtonian law is inconsistent with the postulates of his general relativity theory. On amending the law so as to conform to these postulates, it appears that the orbit of a planet about the sun ought no longer to be a simple ellipse, as it was under the Newtonian law, but rather an ellipse slowly rotating in its own plane. For instance, the orbit of Mercury ought to revolve at a rate of about $42\cdot9''$ per century. Now, for some time one of the outstanding problems of astronomy has been the explanation of the irregularities in the orbit of Mercury. After allowing for all known causes of irregularity, there was found to be outstanding a secular advance of the perihelion, or more simply a slow rotation of the orbit, of amount almost exactly equal to the $42\cdot9''$ per century predicted by the relativity theory of Einstein.

To sum up, then, it is clear that the first of our two clouds has been dissipated by the theory of relativity. This is not surprising, for the theory was in effect designed for this special purpose. But it is important that the cloud has been removed without another one appearing to replace it. Indeed, other clouds have also been removed in the process, such as that surrounding the orbital motion of Mercury. The relativity theory has succeeded, as we have seen, by relegating the ether to a position of absolute unimportance. Whether the ether exists or not we do not and cannot know, but the relativity theory indicates that everything happens exactly as if the ether did not exist. The new theory is concerned with the discovery and formulation of laws rather than with their causes, and so makes no claim to pronounce on the existence of an ether; but it is clear from the experimental evidence of the Michelson-Morley experiment, that if it is finally necessary to call upon an ether to interpret phenomena, this ether will be something quite different

from what we imagined it in the past. In the meantime, the attitude of the relativity theory to the ether is that it has no need for that hypothesis.

The second cloud, over the dynamical theory of heat, is in effect the theorem of Equipartition of Energy, discovered as a mathematical theorem by Maxwell in 1857. The dynamical theory of heat asserts that heat is a mode of motion. Every body has a certain number of capacities of internal motion, or to use the technical term, degrees of freedom, the energy of motion of these degrees of freedom forming what we call the heat of the body. The theorem in question begins by assuming that the motion is determined by laws of the type of Newton's laws of motion, and on this hypothesis it shows that, when any temporary disturbances have passed away, the energy is, so to speak, fairly rationed out amongst the different degrees of freedom. It is not proved that one degree of freedom will have just one ration, but if we take any large group, no matter how selected, their average amount of energy will always be exactly one ration. We can state the matter in a different way by saying that the energy is distributed at random amongst the different degrees of freedom: none of them gets any preferential treatment. The simplest instance of the truth of the theorem is, perhaps, found in the law that the atomic heats of all elements is the same. On the average an atom of silver has just the same energy as an atom of aluminium at the same temperature. The atom of silver is four times as massive as the atom of aluminium, but the energies are made the same by the velocities in silver being just half of those in aluminium.

Another aspect of the meaning of the theorem of equipartition deserves attention. A column of air, say an open organ-pipe of 16 ft. length, can sound not only its own note, but a number of harmonics as well—one in the first octave above the fundamental note, two in the octave above, four, eight, sixteen, and so on, in the succeeding octaves. The degrees of freedom of the air inside the pipe may be thought of as arising from the possibility of motion in space of the molecules of the gas, but they may alternatively be thought of as the possibility of the pipe sounding its fundamental note and all the harmonics, down to those of the very shortest wave-length, comparable with the distances apart of the molecules in the gas. The principle of equipartition now requires that when any exciting agency has died away, and only pure heat-motion remains, the energy shall be distributed equally among all its notes. It can in point of fact be shown by mathematical demonstration that the random heat-motion of the molecules inside the pipe can be resolved into a system of wave-motions such that the fundamental note and all the harmonics have, on the average, exactly the same amount of energy. Thus, so long as the theorem of equipartition remains true, we may regard heat-motion as a musical effect, produced by sounding all the notes which the system is capable of sounding, with equal energy.

A number of instances, such as that of the atomic heats of metals already referred to, prove that the theorem is true in nature, at least within certain limits. But the limits are easily discovered, and it is readily seen that the theorem is not of universal applicability. For example, in the instance just taken, the atom of silver has four times as many electrons in its structure as the atom of aluminium, so that its internal structure has four times as many degrees of freedom. Why, then, does it not get four times as much energy? This and similar cases of failure of the theorem formed the cloud over the dynamical theory of heat.

A good deal of information can be obtained by investigating in what ways the energy is distributed in the cases in which the theorem

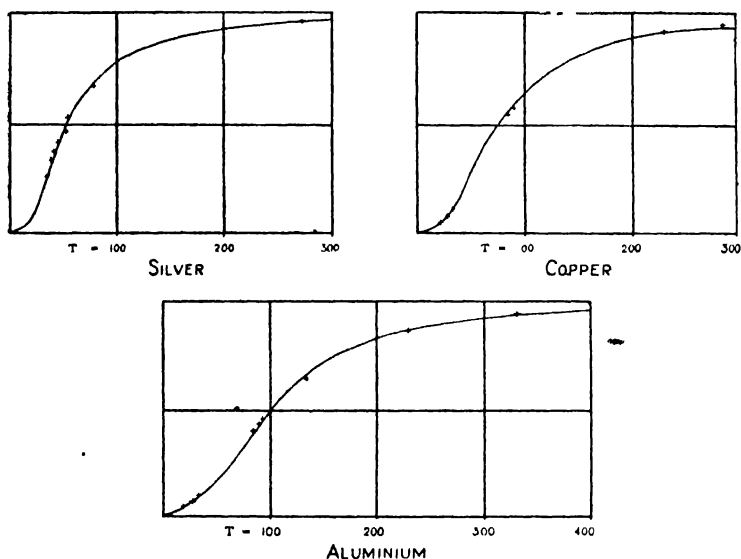


FIG 1.

of equipartition is found to fail. In the case of solid elements such as silver and aluminium, it is found that all the heat-energy resides in the motions of the atoms as a whole; the internal motions of the electrons get none at all. The same is true in a monatomic gas, such as helium or mercury vapour, as is shown by the fact that the ratio of specific heats is $1\frac{2}{3}$. In a diatomic gas at ordinary temperatures, three-fifths of the total energy resides in the motion of translation of the molecules, while the whole of the remaining two-fifths resides either in the motion of rotation of the molecules or in

the to-and-fro motion of the two atoms of which the molecule is formed, probably the latter.

The instances so far mentioned are sharply divided into cases of complete success of the theorem and case of complete failure. But every scientific investigator will recognise that our chances of unravelling the causes of failure will be enormously improved if we can find a case of gradual transition from truth to failure.

An interesting case of failure of exactly this kind has been disclosed by recent investigations on specific heats at low temperature. If the principle of equipartition held, even as regards the atomic motions in a solid, the atomic heats ought to be the same for all elements. They are so at high temperatures, but there is a steady falling off as the temperature decreases. The specific heats of silver, copper, and aluminium at low temperatures, as measured by Nernst and Lindemann, are shown in Fig. 1.

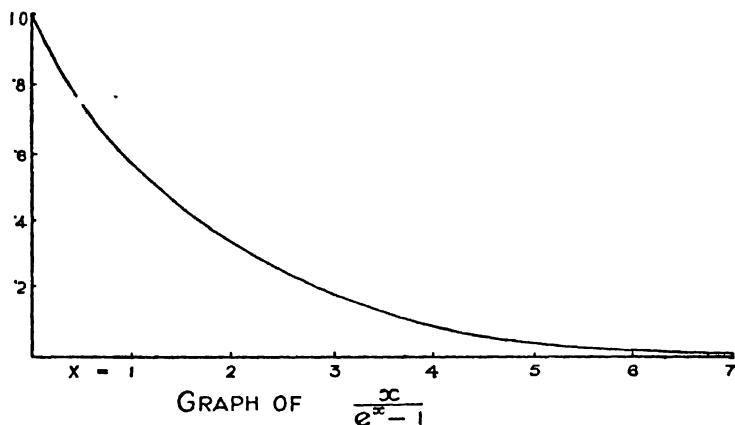


FIG. 2.

Debye, attacking the question mathematically, has shown that the observed values of the specific heats, both for these and other substances, are exactly what they would be if the energy were not rationed out equally amongst the different waves, as demanded by the principle of equipartition, but according to the law

$$\frac{x}{e^x - 1}$$

where x stands for $h\nu/RT$, ν being the frequency of the vibration, T the absolute temperature, and R and h being constants. Fig. 3 shows the theoretical curve deduced by Debye from this law, together with the observed values of Nernst and Lindemann for three

elements. We now see that in heat motion at low temperatures the "sound" is one in which all harmonics do not sound with equal energy; the higher harmonics get nothing like the share of energy allotted to them by the theorem of equipartition, and the energy tends to concentrate in the vibrations of lowest frequency.

The formula just given has the very special significance that it also expresses the partition of energy amongst the different vibrations in the spectrum of a normal black body, as given by the well-known and now generally-accepted formula of Planck. Indeed, it is

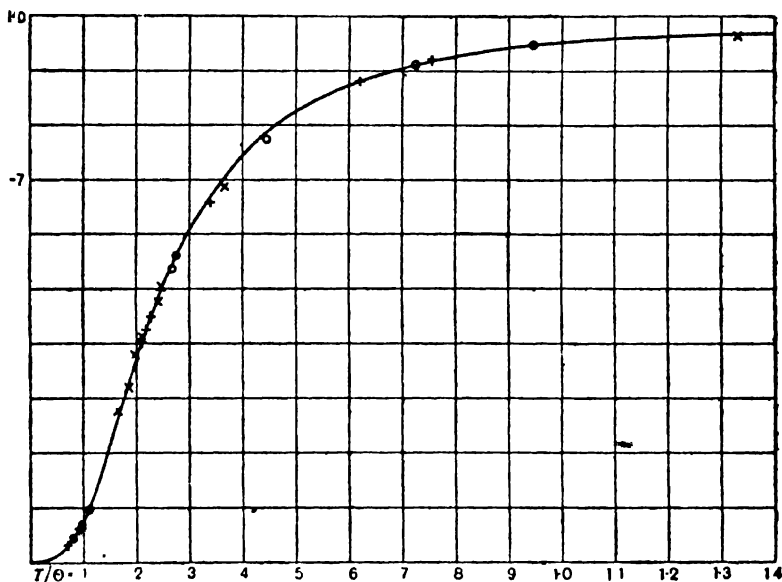


FIG 3.

ATOMIC HEATS AT LOW TEMPERATURES (+ ALUMINIUM, o COPPER, x SILVER).

probable that for dynamical reasons the partition of energy in the black body spectrum must form an indicator of the partition of energy in the black body itself, out of which the spectrum originates. Planck has proved that this is necessarily the case; but his argument is weakened, and to some extent invalidated, by the circumstance that the proof is based on the Newtonian laws of motion which we are now discarding.

In general, however, we may say that in every case examined the partition of energy in vibratory motions of all kinds must be supposed to be that given by the above formula. When x is small,

covering the case of slow vibrations, the formula is of unit value, and the partition is one of equality; on the other hand, the formula shows that vibrations of high frequency get no energy at all, so that here we get the extreme case of failure of the law of equipartition. It is extremely important for us that the theorem does fail in this way, because if all the heat energy in the world were to distribute itself equally over all the degrees of freedom in the world, as required by the theorem of equipartition of energy, everything would become frozen and dead within a small fraction of a second.

Although the view has been opposed in the past, there is now, I think, no room for doubt that the failure of the theorem of equipartition of energy must be interpreted in the most obvious and direct way. The theorem is true subject only to the assumption that the motion is governed by Newton's laws; as a matter of experiment the theorem is found not to be true of high-frequency vibrations; therefore the motion of high-frequency vibrations is not governed by Newton's laws. We must search for a new system of dynamical laws which shall give the observed partition of energy.

The formula $x/(e^x-1)$, which is believed to give the true partition of energy, was originally deduced by Planck from theoretical considerations; but the underlying conceptions were of such a strange and novel nature that at first they gained but little credence. But when the law of partition is known, it becomes merely a mathematical problem to discover what laws of motion will result in this law of partition. In 1911 I showed that this law of partition could only result from laws substantially identical with those already assumed by Planck. Shortly after, Poincaré announced the same result, with the important addition that the main nature of the laws would not be altered by a slight variation in the observed law of partition. Planck had assumed that energy was transmitted not by continuous processes but by a system of jumps and jerks. It appears that the mere fact that the energy is not divided equally among the different vibrations is sufficient to show that there must be discontinuities of some kind in the fundamental laws of motion. The particular type of discontinuity which is found necessary to lead to the observed formula $x/(e^x-1)$ is expressed by Planck's equation

$$\epsilon = h\nu.$$

Here h is the same constant as occurs in the value of x , ν is the frequency of the vibration in question, and ϵ , equal to $h\nu$, is found to be of the same physical dimensions as energy, and may be spoken of as the "quantum" of energy associated with a vibration of frequency ν . The law of discontinuity is such that the vibration can only gain or lose energy by whole quanta. Thus a vibration of frequency ν may have no energy at all, or one quantum, or two quanta, but cannot for instance have half a quantum or $1\frac{1}{2}$ quanta—the energy changes by discontinuous jumps.

It appears, then, that we are brought to the contemplation of a universe in which the ultimate motion is of a discontinuous nature. The supposed continuity of nature must be only an illusion ; motion when seen on a large scale is continuous, but is resolved into discontinuity when we imagine it viewed under a sufficiently high-powered microscope. Such revolutionary conceptions will be made mentally more palatable to us if we can find direct evidence of the "jumps" in question, and a good deal of such evidence exists.

Perhaps the most striking, although not the most direct, evidence is provided by Bohr's theory of line-spectra. We know from the researches of Rutherford that the hydrogen atom consists of two constituents—a positive electron and a negative electron—circling round one another. Bohr assumes that only a limited number of orbits are possible ; the two electrons may circle at distances such that the motion possesses one, two, or any integral number of the quanta of energy corresponding to the frequency of rotation, but at no other distances. Sudden drops from one of these distances to another can take place, and when this happens the energy set free leaves the atom in the form of one quantum of monochromatic light, the frequencies of these bundles of light giving the line-spectrum. The line-spectrum has always defied interpretation in terms of the old mechanics ; indeed, the old mechanics made it impossible that a line-spectrum could occur at all. Bohr's theory has given a brilliant explanation ; his theory predicted the position of the lines exactly, and further predicted the existence of other lines in the infra-red which were not known to him when he published his theory, but were subsequently discovered by Lyman. The theory also predicted a large part of the helium spectrum, and a comparison of this spectrum with that of hydrogen enabled Fowler to determine the mass of the electron to an accuracy at least equal to that of the best of previous determinations.

Einstein has supposed that when the quantum of energy is set free in the form of radiation from radiating matter it does not spread out in space, but remains as a compact bundle of energy. We must, on this view, think of radiation not as waves spreading out in a sea of ether, but perhaps rather as fishes swimming out into a sea of—we do not know what. If this is so, we might be able to obtain very direct evidence of the existence of these fishes by spreading nets to catch them. Suppose we spread nets of varying meshes, say two, four, six, eight inches, and set free what the quantum theory tells us ought to be five-inch fishes, and what the old mechanics tells us ought to be waves in our sea. Suppose we find that the six-inch and eight-inch nets are unaffected, while the two and four-inch nets show holes in each case of five inches. Suppose further that millions of what the quantum theory pronounces to be one-inch fishes have no effect, while even the smallest number of what the quantum theory calls three and five-inch fishes are found to make holes of the corre-

sponding size—shall we not be justified in supposing that we are not altogether on the wrong track in believing that the fishes really exist?

Allowing for the necessary imperfections of an analogy, evidence of the kind just described is provided by the photo-electric effect. High-frequency light falling on a clean metallic surface breaks up the atoms of the metal, the breakage being shown by the liberation of electrons. The energy required to liberate an electron from an atom of any given metal is known from other sources—this corresponds to the mesh of the net; in addition to this, the electron brings away with it a certain amount of kinetic energy. On adding this to the energy required to liberate the electron we invariably obtain one quantum of energy of the frequency of the incident light. If the light is of frequency such that one quantum is less than the energy required to liberate an electron we may allow the light to fall on the metallic surface for years, and no atoms are broken up, no matter how intense the light, while even the feeblest light, if of sufficiently high frequency, will at once start to liberate electrons.

Such phenomena as the photo-electric effect and the line-spectra of the elements are quite inexplicable in terms of the old dynamics, while they receive such complete and convincing explanations in terms of the quantum-theory that we might be inclined to jump to the conclusion that the quantum-theory contained the whole truth and nothing but the truth. On the other hand, all interference-phenomena and phenomena of reflection, polarisation, etc., receive a simple explanation in terms of the old dynamics, and seem at present inexplicable in terms of the new. It seems impossible to reconcile the new quantum-theory with the old undulatory theory of light. There is a very real difficulty here; indeed, it constitutes the big outstanding puzzle of present-day physics. The evidence of interference suggests that light must be continuous and almost infinitely divisible, while the evidence of the photo-electric effect is that light consists of discrete "quanta" which are discontinuous and completely indivisible.

No solution has yet been found; one has hardly been suggested. It may perhaps be worthy of notice that the theory of relativity is also to some extent antagonistic to the undulatory theory of light, for when the medium through which the waves were supposed to be propagated is abolished, the waves themselves reduce to little more than a mathematical fiction, and the undulatory theory of light reduces to the solution of a differential equation. In the past the waves in the ether have been regarded as the ultimate reality, while the differential equation has been regarded merely as a means of calculating the motion of the wave. Perhaps the scientist of the future will regard the differential equation as the ultimate reality, while the whole mechanism of the undulatory theory—ether, forces, waves, interference, etc.—will be regarded as an extraordinarily

cumbersome nineteenth century model to represent the phenomena demanded by the differential equation ; the differential equation will be regarded as determining the changes of the inanimate parts of the universe except under certain conditions, which we speak of as the presence of matter, where the differential equation will yield to an equation of finite differences—the expression of the complete quantum-theory. These speculative reflections may indicate the direction in which a solution of the difficulty may perhaps ultimately be found, but they are very far from supplying this solution.

[J. H. J.]

Friday, May 11, 1917.

SIR JAMES CRICHTON-BROWNE, J.P. M.D. LL.D. D.Sc. F.R.S.,
Treasurer and Vice-President, in the Chair.

PROFESSOR JOHN JOLY, M.A. D.Sc. F.R.S.

Radioactive Haloes.

THESE minute objects have long been known to petrologists, but their explanation is of recent date. They are formed around particles containing radioactive matter and are caused by an effect of the alpha radiations on certain minerals of the ferro-magnesium group. Radioactive haloes may, therefore, be derived from uranium or thorium, and the series of alpha-ray changes characteristic of the radioactive transformations originated by these parent substances determine the dimension and structure of the halo. It is easy to refer a well developed halo to one or other of these parent substances.

The uranium series of elements gives rise to eight alpha-ray emitting substances, each of special and characteristic range. The thorium series of elements gives rise to seven alpha-rays of characteristic range. It is found that when the integral ionization of these rays, as defined by the Bragg curve of ionization for each ray, is determined by the simple process of adding the ordinates of the eight or seven several curves plotted to the same axes of reference, the two resulting curves (i.e. that for the uranium series and that for the thorium series) agree with the features of uranium and thorium haloes.

But in order to account for the mode of development of the halo, i.e. the sequence in which its several features appear, it is further necessary to assume that some cause exists which favours the development of the outer features, or in other words counteracts the weakening of the ionization arising from the spreading of the rays from the radioactive nucleus of the halo. In it is found that the inner ring which marks the first beginning of the halo may be attended by the appearance of the outermost ring due to the alpha-ray of greatest range; an effect which should not occur if the ionization intensity fell off with the divergence of the rays, as might be expected. The explanation offered is that the halo-genesis follows similar laws to those governing photographic effects, so that repetition of stimuli leads to reversal of the earlier effects. Reversal will therefore be less active as the rays diverge outwards, and herein is

found a reason for the relative accentuation of the ionization due to the rays of longest range. Haloes presenting all the appearance of more complete reversal have been observed.

The foregoing principles satisfactorily explain the features, dimensions, and order of formation of haloes formed around radioactive centres.

A third type of halo is observed which is referable to the emanation of radium as parent substance. This halo appears generally in connexion with conduits in which there is plain evidence that radioactive gas or liquid has at one time circulated. The nucleus of the halo has apparently absorbed the emanation, and the further changes of this substance, giving rise to four characteristic alpha-rays, have sufficed to form a halo which finds, in its every feature, explanation according to the principles outlined above.

There is some degree of misfit in the primal rings of both the thorium and the uranium halo. In the case of the thorium halo this misfit is very minute, but is sufficient to suggest that the range generally accepted for the thorium alpha-ray is a little excessive. This agrees with the indication of the Geiger-Nuttall curve, connecting range and period of transformation. In the case of the primal ring of the uranium halo—which is largely due to the ionization arising from U_1 and U_2 —the misfit is more conspicuous, and is in the opposite sense to the misfit of the thorium ray. The observed halo-ring indicates a former range greater than what is now observed.

Until this misfit is shown to be confined to halves of Palæozoic or Archæan ages it seems premature to advance any explanation of it. It is worth noting, however, that a former longer range of the ray of U_1 , and hence a more rapid rate of decay of uranium in early times, would explain the disagreement of the lead-ratio of the uranium series with that of the thorium series, and concurrently would reconcile radioactive methods of determining the earth's age with those based on the indications of denudative effects.

[J. J.]

Friday, May 18, 1917.

SIR WILLIAM PHIPSON BEALE, BART., K.C. M.P.,
Vice-President, in the Chair.

PROFESSOR FREDERICK SODDY, M.A. F.R.S.

The Complexity of the Chemical Elements.

THE elements of the chemist are now known to be complex in three different senses. In the first sense the complexity is one that concerns the general nature of matter, and therefore of all the elements in common to greater or less degree. It follows from the relations between matter and electricity which have developed gradually during the past century as the result of experiments made and theories born within the four walls of this Institution. Associated initially with the names of Davy and Faraday, they have only in these days come to full fruition as the result of the very brilliant elucidation of the real nature of electricity by your distinguished Professor of Physics, Sir Joseph Thomson. Such an advance, developing slowly and fitfully, with long intervals of apparent stagnation, needs to be reviewed from generation to generation, disentangled from the undergrowth that obscures it, and its clear conclusions driven home. This complexity of the chemical elements is a consequence of the condition that neither free electricity nor free matter can be studied alone, except in very special phenomena. Our experimental knowledge of matter in quantity is necessarily confined to the complex of matter and electricity which constitutes the material world. This applies even to the "free" elements of the chemist, which in reality are no more free than they are in their compounds. The difference is merely that, whereas in the latter the elements are combined with other elements, in the so-called free state they are combined with electricity. I shall touch but briefly on this first aspect, as in principle it is now fairly well understood. But its consistent and detailed application to the study of chemical character is still lacking.

The second sense in which the elements, or some of them at least, are known now to be complex has, in sharp contrast to the first, developed suddenly and startlingly from the recognition in radio-active changes, of different radio-elements, non-separable by chemical

means, now called isotopes. The natural corollary of this is that the chemical element represents rather a type of element, the members of the type being only chemically alike. Alike they are in most of those properties, which were studied prior to the last decade of last century and which are due, as we now think, to the outer shells of the atom, so alike that all the criteria, hitherto relied upon by the chemist as being the most infallible and searching, would declare them to be identical. The apparent identity goes even deeper into the region reached by X-ray spectrum analysis which fails to distinguish between them. The difference is found only in that innermost region of all, the nucleus of the atom, of which radioactive phenomena first made us aware.

But, though these phenomena pointed the way, and easily showed to be different what the chemist and spectroscopist would have decided to be identical, it did more. It showed that although the finer and newer criteria, relied upon by the chemist in his analysis of matter, must of necessity fail in these cases, being ultimately electrical in character, yet the difference should be obvious in that most studied and distinctive characteristic of all—the criterion by which Dalton first distinguished the different kinds of atoms—the atomic weight. Those who have devoted themselves to the exact determination of these weights have now confirmed the difference in two separate cases, which, in absence of what perhaps they might regard as “preconceived notions,” they were unable to discover for themselves. This is the experimental development to which I wish more especially to direct your attention. It indicates that the chemical analysis of matter is, even within its own province, superficial rather than ultimate, and that there are indefinitely more distinct elements than the ninety-two possible types of element accommodated by the present periodic system.

The third sense in which the elements are known to be complex is that which, in the form of philosophical speculations, has come down to us from the ancients, which inspired the labours of the alchemists of the Middle Ages, and which in the form of Prout's hypothesis has re-appeared in scientific chemistry. It is the sense that denies to Nature the right to be complex, and from the earliest times, faith out-stripping knowledge, has underlain the belief that all the elements must be built up of the same primordial stuff. The facts of radioactive phenomena have shown that all the radio-elements are indeed made up out of lead and helium, and this has definitely removed the question from the region of pure speculation. We know that helium is certainly a material constituent of the elements in the Proutian sense, and it would be harmless, if probably fruitless, to anticipate the day of fuller knowledge by atom building and unbuilding on paper. Apart altogether from this, however, the existence of isotopes, the generalisation concerning the Periodic Law that has arisen from the study of radioactive change on the one

hand and the spectra of X-rays on the other, and experiments on the scattering of α -particles by matter, do give us for the first time a definite conception as to what constitutes the difference between one element and another. We can say how gold would result from lead or mercury, even though the control of the processes necessary to effect the change still eludes us. The nuclear atom proposed by Sir Ernest Rutherford, even though, admittedly, it is only a general and incomplete beginning to a complete theory of atomic structure, enormously simplifies the correlation of a large number of diverse facts. This and what survives of the old electronic theory of matter, in so far as it attempted to explain the Periodic Law, will therefore be briefly referred to in conclusion.

THE FREE ELEMENT A COMPOUND OF MATTER AND ELECTRICITY.

Although Davy and Faraday were the contemporaries of Dalton, it must be remembered that it took chemists fifty years to put the atomic theory on a definite and unassailable basis, so that neither of these investigators had the benefit of the very clear view we hold to-day. Davy was the originator of the first electro-chemical theory of chemical combination, and Faraday's dictum, "the forces of chemical affinity and electricity are one and the same," it is safe to say, inspires all the modern attempts to reduce chemical character to a science in the sense of something that can be measured quantitatively, as well as expressed qualitatively. Faraday's work on the laws of electrolysis and the discovery that followed from it, when the atomic theory came to be fully developed, that all monovalent atoms or radicles carry the same charge, that divalent atoms carry twice this charge and so on, can be regarded to-day as a simple extension of the law of multiple proportions from compounds between matter and matter to compounds between matter and electricity. Long before the electric charge had been isolated, or the properties of electricity divorced from matter discovered, the same law of multiple proportions which led, without any possibility of escape, to an atomic theory of matter, led, as Helmholtz pointed out in his well-known Faraday lecture to the Chemical Society in this Theatre in 1881, to an atomic theory of electricity.

The work of Hittorf on the migration of ions, the bold and upsetting conclusion of Arrhenius that in solution many of the compounds hitherto regarded as most stable exist dissociated into ions, the realisation that most of the reactions that take place instantaneously, and are utilised for the identification of elements in chemical analysis, are reactions of ions rather than of the element in question, made very familiar to chemists the enormous difference between the properties of the elements in the charged and in the electrically neutral state.

More slowly appreciated, and not yet perhaps sufficiently emphasized, was the unparalleled intensity of these charges in comparison with anything that electrical science can show, which can be expressed tritely by the statement that the charge on a milligram of hydrogen ions would raise the potential of the world 100,000 volts. Or, if we consider another aspect, and calculate how many free hydrogen ions you could force into a bottle without bursting it, provided, of course, that you could do so without discharging the ions, you would find that, were the bottle of the strongest steel, the breech of gun, for example, it would burst, by reason of the mutual repulsion of the charges, before as much was put in as would, in the form of hydrogen gas, show the spectrum of the element in a vacuum tube.

Then came the fundamental advances in our knowledge of the nature of electricity, its isolation as the electron, or atom of negative electricity, the great extension of the conception of ions to explain the conduction of electricity through gases, the theoretical reasoning, due in part to Heaviside, that the electron must possess inertia inversely proportional to the diameter of the sphere on which it is concentrated by reason of the electro-magnetic principles discovered by Faraday, leading to the all-embracing monism that all mass may be of electro-magnetic origin.

This put the coping-stone to the conclusion that the elements as we apprehend them in ordinary matter are always compounds. In the "free" state they are compounds of the element in multiple atomic proportions with the electron. The ions, which are the real chemically uncombined atoms of matter, can no more exist free in quantity than can the electrons.

The compound may be individual as between the atom and the electron, or it may be statistical, affecting the total number merely of the opposite charges, and the element presumably will be an insulator or conductor of electricity accordingly. Analogously, with compounds, the former condition applies to unionised compounds such as are met with in the domain of organic chemistry, or ionised, as in the important classes of inorganic compounds, the acids, bases and salts. Just as the chemist has long regarded the union of hydrogen and chlorine as preceded by the decomposition of the hydrogen and chlorine molecule, so he should now further regard the union itself as a decomposition of the hydrogen atom into the positive ion and the negative electron, and a combination of the latter with the chlorine atom.

One of the barriers to the proper understanding and quantitative development of chemical character from this basis is, perhaps, the conventional idea derived from electrostatics, that opposite electric charges neutralise one another. In atomic electricity or chemistry, though the equality of the opposite charges is a necessary condition for existence, there is no such thing as neutralisation, or the elec-

trically neutral state. Every atom being the seat of distinct opposite charges, intensely localised, the state of electric neutrality can apply only to a remote point outside it, remote in comparison with its own diameter. We are getting back to the conception of Berzelius, with some possibility of understanding it, that the atom of hydrogen, for example, may be strongly electro-positive, and that of chlorine strongly electro-negative, with regard to one another, and yet each may be electrically neutral in the molar sense. Some day it may be possible to map the electric field surrounding each of the ninety-two possible types of atom, over distances comparable with the atomic diameter. Then the study of chemical character would become a science in Kelvin's sense, of something that could be reduced to a number. But the mathematical conceptions and methods of attack used in electrostatics for macroscopic distances are ill-suited for the purposes of chemistry, which will have to develop methods of its own.

We have to face an apparent paradox that the greater the affinity that binds together the material and electrical constituents of the atom, the less is its combining power in the chemical sense. In other words, the chemical affinity is in inverse ratio to the affinity of matter for electrons. The helium atoms offer a very simple and instructive case. Helium is non-valent and in the zero family, possessing absolutely no power of chemical combination that can be detected. Yet we know the atom possesses two electrons, for in radioactive change it is expelled without them as the α -particle. The discharge of electricity through it and positive-ray analysis show that the electrons, or certainly one of them, are detachable by electric agencies, although not by chemical agencies. One would expect helium to act as a diad, forming helides analogous to oxides.

Professor Armstrong for long advocated the view that these inert gases really are endowed with such strong chemical affinities that they are compounds that have never been decomposed. They certainly have such strong affinities for electrons that the atom, the complex of the + ion and electrons, cannot be decomposed chemically. Yet, in this case, where the affinity of the matter for the electron is at a maximum, the chemical combining power is absent.

These gases seem to furnish the nearest standard we have to electric neutrality in the atomic sense. The negative charge of the electrons exactly satisfies the positive charge of the matter, and the atomic complex is chemically, because electrically, neutral. In the case of the electro-positive elements, hydrogen and the alkali-metals, one electron more than satisfies the positive charge on the ion, and so long as the equality of opposite charges is not altered, the electron tries to get away. In the case of the electro-negative elements, such as the halogens, the negative charge, though equal presumably to the positive, is not sufficient to neutralise the atom. Hence these groups show strong mutual affinity, one having more

and the other less negative electricity than would make the system atomically neutral like helium. The electron explains well the merely numerical aspect of valency. But chemical combining power itself seems to require the idea that equal and opposite charges in the atomic sense are only exactly equivalent in the case of the inert gases. None of these ideas are now new, but their consistent application to the study of chemical compounds seems curiously to hang fire, as though something were still lacking.

It is so difficult for the chemist consistently to realise that chemical affinity is due to a dissociating as well as to a combining tendency and is a differential effect. There is only one affinity, probably, and it is the same as that between oppositely charged spheres. But, atomic charges being enormous and the distances over which they operate in chemical phenomena being minute, this affinity is colossal, even in comparison with chemical standards. What the chemist recognises as affinity is due to relatively slight differences between the magnitude of the universal tendency of the electron to combine with matter in the case of the different atoms. Over all, is the necessary condition that the opposite charges should be equivalent, but this being satisfied, the individual atoms display the tendencies inherent in their structure, some to lose, others to gain electrons, in order, as we believe from Sir Joseph Thomson's teaching, to accommodate the number of electrons in the outermost ring to some definite number. Chemical affinity needs that some shall lose as well as others gain. Chemical union is always preceded by a dissociation. The tendency to combine, only, is specific to any particular atom, but the energy and driving power of combination is the universal attraction of the + for the - change, of matter for the electron.

THE ELECTRICAL THEORY OF MATTER.

Another barrier that undoubtedly exists to the better appreciation of the modern point of view, even among those most willing to learn, is the confusion that exists between the earlier and the present attempt to explain the relation between matter and electricity. We know negative electricity apart from matter as the electron. We know positive electricity apart from the electron, the hydrogen ion and the radiant helium atom or α -particle of radioactive change for example, and it is matter in the free or electrically uncombined condition. Indeed, if you want to find matter free and uncombined, the simple elementary particle of matter in the sense of complexity being discussed, you will go, paradoxically, to what the chemist terms a compound rather than to that which he terms the free element. If this compound is ionised completely it constitutes the nearest approach to matter in the free state. Thus all acids owe their common acidic quality to really free hydrogen, the hydrogen ion, a

particle more different from the hydrogen atom than the atom is from the hydrogen molecule.

Positive electricity is thus emphatically not the mere absence of electricity, and any electrical theory of matter purporting to explain matter in terms of electricity does so by the palpable sophistry of calling two fundamentally different things by the same name. The dualism remains whether you speak of matter and electricity, or of positive and negative electricity, and the chemist would do well to stick to his conception of matter, until the physicist has got a new name for positive electricity which will not confuse it with the only kind of electricity that can exist apart from matter.

On the other hand, the theory of the electro-magnetic origin of mass or inertia is a true monism. It tries to explain consistently two things—the inertia of the electron and the inertia of matter—by the same cause. The inertia of the former being accounted for by the well-known electro-magnetic principles of Faraday, by the assumption that the charge on the electron is concentrated into a sphere of appropriate radius; the 2000-fold greater inertia of the hydrogen ion, for example, can be accounted for by shrinking the sphere to one-two-thousandth of the electronic radius.

But the electrical dualism remains completely unexplained. Call the electron *E* and the hydrogen ion *H*. The facts are that two *E*'s repel one another with the same force and according to the same law as two *H*'s repel each other, or as an *H* attracts an *E*. These very remarkable properties of *H* and *E* are not explained by the explanation of the inertia. Are *E* and *H* made up of the same stuff or of two different stuffs? We do not know, and certainly have no good reason to assume, that matter minus its electrons is made of the same thing as the electron. We have still to reckon with two different things.

THE CHEMICAL ELEMENTS NOT NECESSARILY HOMOGENEOUS.

I pass now to the second and most novel sense in which the elements, or some of them at least, are complex. In their discovery of new radioactive elements, M. and Mme. Curie used radioactivity as a method of chemical analysis precisely as Bunsen and Kirchhoff, and later Sir William Crookes, used spectrum analysis to discover caesium and rubidium, and thallium. The new method yielded at once, from uranium minerals, three new radio-elements, radium, polonium and actinium. According to the theory of Sir Ernest Rutherford and myself, these elements are intermediate members in a long sequence of changes of the parent element uranium. In a mineral the various members of the series must co-exist in equilibrium, provided none succeed in escaping from the mineral, in quantities inversely proportional to their respective rates of change, or directly proportional to their periods of average life. Radium

changes sufficiently slowly to accumulate in small but ponderable quantity in a uranium mineral, and so it was shown to be a new member of the alkaline-earth family of elements, with atomic weight 226.0, occupying a vacant place in the Periodic Table. Polonium changes 4500 times more rapidly, and can only exist to the extent of a few hundredths of a milligram in a ton of uranium mineral. Actinium also, though its life period is still unknown, and very possibly is quite long, is scarce for another reason, that it is not in the main line of disintegration, but in a branch series which claims only a few per cent of the uranium atoms disintegrating. In spite of this, polonium and actinium have just as much right to be considered new elements, probably, as radium has. Polonium has great resemblances in chemical character both to bismuth and tellurium, but was separated from the first by Mme. Curie and from the second by Marckwald. In the position it occupies as the last member of the sulphur group, bismuth and tellurium are its neighbours in the Periodic Table. Actinium resembles the rare-earth elements, and most closely lanthanum, but an enrichment of the proportion of actinium from lanthanum has been effected by Giesel. The smallness of the quantities alone prevents their complete separation in the form of pure compounds as was done for radium.

The three gaseous members, the emanations of radium, actinium and thorium, were put in their proper place in the Periodic Table almost as soon as radium was, for, being chemically inert gases, their characterisation was simple. They are the last members of the argon family, and the fact that there are three of about the same atomic weight was probably the first indication, although not clearly appreciated, that more than one chemical element could occupy the same place in the Periodic Table.

The extension of the three disintegration series proceeded apace; new members were being continually added, but no other new radio-elements—new, that is, in possessing a new chemical character—were discovered. The four longest-lived to be added, radio-lead or radium-D, as it is now more precisely termed, and ionium in the uranium series, and mesothorium-I and radiothorium in the thorium series, could not be separated from other constituents always present in the minerals, radium-D from lead, ionium and radiothorium from thorium, and mesothorium-I from radium. An appreciable proportion of the radioactivity of a uranium mineral is due to radium-D and its products, and its separation would have been a valuable technical achievement, but, though many attempts have made, this has never been accomplished, and, we know now, probably never will be.

Seven years ago it was the general opinion in the then comparatively undeveloped knowledge of the chemistry of the radio-elements, that there was nothing especially remarkable in this. The chemist is familiar with many pairs or groups of elements, the separation of

which is laborious and difficult, and the radio-chemist had not then fully appreciated the power of radioactive analysis in detecting a very slight change in the proportions of two elements, one or both of which were radioactive. The case is not at all like that of the rare-earth group of elements, for example, in which the equivalent or atomic weight is used as a guide to the progress of the separation. Here the total difference in the equivalent of the completely separated elements is only a very small percentage of the equivalent, and the separation must already have proceeded a long way before it can be ascertained.

Human nature plays its part in scientific advances, and the chemist is human like the rest. My own views on the matter developed with some speed when, in 1910, I came across a new case of this phenomenon. Trying to find out the chemical character of mesothorium-I, which had been kept secret for technical reasons, I found it to have precisely the same chemical character as radium, a discovery which was made in the same year by Marckwald, and actually first published by him. I delayed my publication some months to complete a very careful fractional crystallisation of the barium-radium-mesothorium-I chloride separated from thorinite. Although a great number of fractionations were performed, and the radium was enriched, with regard to the barium, several hundred times, the ratio between the radium and mesothorium-I was, within the very small margin of error possible in careful radioactive measurements, not affected by the process. I felt justified in concluding from this case, and its analogy with the several other similar cases then known, that radium and mesothorium-I were non-separable by chemical processes, and had a chemical character not merely like, but identical. It followed that some of the common elements might similarly be mixtures of chemically identical elements. In the cases cited, the non-separable pairs differ in atomic weight from 2 to 4 units. Hence the lack of any regular numerical relationships between the atomic weights would on this view follow naturally. (*Trans. Chem. Soc.* 1911, xcix. 72.) This idea was elaborated in the Chemical Society's Annual Report on Radioactivity for 1910, in the concluding section summing up the position at that time. This was I think the beginning of the conception of different elements identical chemically, which later came to be termed "isotopes," though it is sometimes attributed to K. Fajans, whose valuable contributions to radioactivity had not at that date commenced, and whose first contribution to this subject did not appear till 1913.

In the six or seven years that have elapsed the view has received complete vindication. Really, three distinct lines of advance converged to a common conclusion, and, so far as is possible, these may be disentangled. First, there has been the exact chemical characterisation from the new point of view of every one of the members of the three disintegration series, with lives over one minute.

Secondly, came the sweeping generalisations in the interpretation of the Periodic Law. Lastly, there has been the first beginnings of our experimental knowledge of atomic structure, which got beyond the electronic constituents and at the material atom itself.

In pursuance of the first, Alexander Fleck, at my request, commenced a careful systematic study of the chemical character of all the radio-elements known of which our knowledge was lacking or imperfect, to see which were and which were not separable from known chemical elements. Seldom can the results of so much long and laborious chemical work be expressed in so few words. Every one, that it was possible to examine, was found to be chemically identical either with some common element or with another of the new radio-elements. Of the more important characterisations, mesothorium-II was found to be non-separable from actinium, radium-A from polonium, the three B-members and radium-D from lead, the three C-members and radium-E from bismuth, actinium-D and thorium-D from thallium. These results naturally took some time to complete, and became known fairly widely to others working in the subject before they were published, through A. S. Russell, an old student, who was then carrying on his investigations in radioactivity in Manchester. Their interpretation constitutes the second line of advance.

Before that is considered, it may first be said that every case of chemical non-separability put forward has stood the test of time, and all the many skilled workers who have pitted their chemical skill against Nature in this quest have merely confirmed it. The evidence at the present day is too numerous and detailed to recount. It comes from sources, such as in the technical extraction of mesothorium from monazite, where one process is repeated a nearly endless number of times; from trials of a very great variety of methods, as, for example, in the investigations on radium-D and lead by Paneth and von Hevesy; it is drawn from totally new methods, as in the beautiful proof by the same authors of the electro-chemical identity of these two isotopes; it is at the basis of the use of radioactive elements as indicators for studying the properties of a common element, isotopic with it, at concentrations too feeble to be otherwise dealt with, and from large numbers of isolated observations, as well as prolonged systematic researches. One of the finest examples of the latter kind of work, the Austrian researches on ionium, will be dealt with later. The most recent, which appeared last month, is by T. W. Richards and N. F. Hall, who subjected lead from Australian carnotite, containing therefore radium-D, to over a thousand fractional crystallisations in the form of chloride, without appreciably altering the atomic weight or the β -activity. So that it may be safely stated that no one who has ever really tested this conclusion now doubts it, and after all they alone have a right to an opinion.

This statement of the non-separability by chemical methods of

pairs or groups of elements suffers perhaps from being in a negative form. It looks too much like a mere negative result, a failure, but in reality it is one of the most sweeping positive generalisations that could be made. Ionium we say is non-separable from thorium, but every chemist knows thorium is readily separated from every other known element. Hence, one now knows every detail of the chemistry of the vast majority of these new radio-elements by proxy, even when their life is to be measured in minutes or seconds, as completely as if they were obtainable, like thorium is, by the ton. The difference it makes can only be appreciated by those who have lived through earlier days, when, in some cases dealing with the separation of radio-constituents from complex minerals, after every chemical separation one took the separated parts to the electroscope to find out where the desired constituent was.

As the evidence accumulated that we had to deal here with something new and fundamental, the question naturally arose whether the spectrum of isotopes would be the same. The spectrum is known, like the chemical character, to be an electronic rather than mass phenomenon, and it was to be expected that the identity should extend to the spectrum. The question has been tested very thoroughly by A. S. Russell and R. Rossi in this country, and by the Austrian workers at the Radium Institut of Vienna, for ionium and thorium, and by various workers for the various isotopes of lead. No certain difference has been found, and it may be concluded that the spectra of isotopes are identical. This identity probably extends to the X-ray spectra, Rutherford and Andrada having shown that the spectrum of the γ -rays of radium-B is identical with the X-ray spectrum of its isotope, lead.

THE PERIODIC LAW AND RADIOACTIVE CHANGE.

The second line of advance interprets the Periodic Law. It began in 1911 with the observation that the product of an α -ray change always occupied a place in the Periodic Table two places removed from the parent in the direction of diminishing mass, and that in subsequent changes where α -rays are not expelled the product frequently reverts in chemical character to that of the parent, though its atomic weight is reduced 4 units by the loss of the α -particle, making the passage across the table curiously alternating. Thus the product of radium (Group II) by an α -ray change is the emanation in the zero group, of ionium (Group IV), radium, and so on, while, in the thorium series, thorium (Group IV) produces by an α -ray change mesothorium-I (Group II), which, in subsequent changes in which no α -rays are expelled, yields radio-thorium, back in Group IV again. (Chemistry of the Radio-Elements, p. 29, 1st Edition, 1911.) Nothing at that time could be said about β -ray changes. The products were for the most part very short-lived and imperfectly

characterised chemically, and several lacunæ still existed in the series masking the simplicity of the process. But early in 1913 the whole scheme became clear, and was pointed out first by A. S. Russell, in a slightly imperfect form, independently by K. Fajans from electrochemical evidence, and by myself, in full knowledge of Fleck's results, still for the most part unpublished, all within the same month of February. It was found that, making the assumption that uranium-X was in reality two successive products giving β -rays, a prediction Fajans and Göhring proved to be correct within a month, and a slight alteration in the order at the beginning of the uranium series, every α -ray change produced a shift of place as described, and every β -ray change a shift of one place in the opposite direction. Further and most significantly, when the successive members of the three disintegration series were put in the places in the table dictated by these two rules, it was found that all the elements occupying the same place were those which had been found to be non-separable by chemical processes from one another, and from the element already occupying that place, if it was occupied, before the discovery of radioactivity. For this reason the term "isotope" was coined to express an element chemically non-separable from the other, the term signifying "the same place."

So arranged, the three series extended from uranium to thallium, and the ultimate product of each series occupied the place occupied by the element lead. The ultimate products of thorium should, because six α -particles are expelled in the process, have an atomic weight 24 units less than the parent, or about 208. The main ultimate product of uranium, since eight α -particles are expelled in this case, should have the atomic weight 206. The atomic weight of ordinary lead is 207.2, which made it appear very likely that ordinary lead was a mixture of the two isotopes, derived from uranium and thorium. The prediction followed that lead, separated from a thorium mineral, should have an atomic weight about a unit higher, and that separated from uranium minerals about a unit lower, than the atomic weight of common lead, and in each case this has now been satisfactorily established.

THE ATOMIC WEIGHT OF LEAD FROM RADIOACTIVE MINERALS.

It should be said that Boltwood and also Holmes had, from geological evidence, both decided definitely against it being possible that lead was a product of thorium, because thorium minerals contain too little lead, in proportion to the thorium, to accord with their geological ages. Whereas, the conclusion that lead was the ultimate product of the uranium series had been thoroughly established by geological evidence, and has been the means, in the hands of skilful investigators, of ascertaining geological ages with a degree of pre-

cision not hitherto possible. Fortunately I was not deterred by the *non possumus*, for it looks as if everybody was right! An explanation of this paradox will later be attempted. In point of fact, there are exceedingly few thorium minerals that do not contain uranium, and since the rate of change of uranium is about 2.6 times that of thorium, one part of uranium is equal as a lead-producer to 2.6 parts of thorium. Thus Ceylon thorianite, one of the richest of thorium minerals, containing 60 to 70 per cent of ThO_2 , may contain 10 to 20 and even 30 per cent of U_3O_8 , and the lead from it may be expected to consist of very similar quantities of the two isotopes, to be in fact very similar to ordinary lead. I know of only one mineral which is suitable for this test. It was discovered at the same time as thorianite, and from the same locality—Ceylon thorite, a hydrated silicate containing some 57 per cent of thorium and 1 per cent of uranium only. In the original analysis no lead was recorded, but I found it contained 0.4 per cent, which, if it were derived from uranium only, would indicate a very hoary ancestry, comparable, indeed, with the period of average life of uranium itself. On the other hand, if (1) all the lead is of radioactive origin, (2) is stable, and (3) is derived from both constituents, as the generalisation being discussed indicated, this 0.4 per cent of lead should consist 95.5 per cent of the thorium isotope and 4.5 per cent of the uranium isotope. Thorite thus offered an extremely favourable case for examination.

In preliminary experiments in conjunction with H. Hymn, in which only a gram or less of the lead was available, the atomic weight was found relatively to ordinary lead to be perceptibly higher, and the difference, rather less than one-half per cent, was of the expected order.

I was so fortunate as to secure a lot of 30 kilos. of this unique mineral, which was first carefully sorted, piece by piece, from admixed thorianite and doubtful specimens. From the 20 kilos. of first grade thorite, the lead was separated, purified, reduced to metal, and cast *in vacuo* into a cylinder, and its density determined together with that of a cylinder of common lead similarly purified and prepared. Sir Ernest Rutherford's theory of atomic structure, to be dealt with in the latter part of this discourse, and the whole of our knowledge as to what isotopes were, made it appear probable that their atomic volumes, like their chemical character and spectra, should be identical, and therefore that their density should be proportional to their atomic weight. The thorite lead proved to be 0.26 per cent denser than the common lead. Taking the figure 207.2 for the atomic weight of common lead, the calculated atomic weight of the specimen should be 207.71.

The two specimens of lead were fractionally distilled *in vacuo*, and a comparison of the atomic weights of the two middle fractions made by a development of one of Stas's methods. The lead was converted into nitrate in a quartz vessel, and then into chloride by a

current of hydrogen chloride, in which it was heated at gradually increasing temperature to constant weight. Only single determinations have been done, and they gave the values 207·20 for ordinary lead, and 207·694 for the thorite lead, figures that are in the ratio of 100 to 100·24. This therefore favoured the conclusion that the atomic volume of isotopes is constant.

At the request of Mr. Lawson, interned in Austria, and continuing his researches at the Radium Institut under Prof. Stefan Meyer, the first fraction of the distilled thorite lead was sent him, so that the work could be checked. He reports that Professor Hönigschmid has carried through an atomic weight determination by the silver method, obtaining the value $207\cdot77 \pm 0\cdot014$, as the mean of eight determinations. Hence, the conclusion that the atomic weight of lead derived from thorite is higher than that of common lead has been put beyond reasonable doubt.

Practically simultaneously with the first announcement of these results for thorium lead, a series of investigations were published on the atomic weight of lead from uranium minerals, by T. W. Richards and collaborators at Harvard, Maurice Curie in Paris, and Hönigschmid and collaborators in Vienna, which show that the atomic weight is lower than that of ordinary lead. The lowest result hitherto obtained is 206·046, by Hönigschmid and Mlle. Horovitz for the lead from the very pure crystallised pitchblende from Morogoro (German East Africa), whilst Richards and Wadsworth obtained 206·085 for a carefully selected specimen of Norwegian cleveite. Numerous other results have been obtained, as, for example, 206·405 for lead from Joachimsthal pitchblende, 206·82 for lead from Ceylon thorianite, 207·08 for lead from monazite, the two latter being mixed uranium and thorium minerals. But the essential proportion between the two elements has not, unfortunately, been determined. Richards and Wadsworth have also examined the density of their uranium lead. In every case they have been able to confirm the conclusion that the atomic volume of isotopes is constant, the uranium lead being as much lighter as its atomic weight is smaller than common lead. Many careful investigations of the spectra of these varieties of lead show that the spectrum is absolutely the same so far as can be seen.

THORIUM AND IONIUM.

A second quite independent case of a difference in atomic weight between isotopes has been established. It concerns the isotopes thorium and ionium, and it is connected in an important way with the researches which, on two previous occasions, I have given an account of here, the researches on the growth of radium from uranium, which have been in progress now for fourteen years. It is the intervention of ionium and its very long period of life which has

made the experimental proof of the production of radium from uranium such a long piece of work. Previously only negative results were available. One could only say, from the smallness of the expected growth of radium, that the period of average life of ionium must be at least 100,000 years, forty times longer than that of radium, and, therefore, that there must be at least forty times as much ionium by weight as radium in uranium minerals, or at least 13.6 grams per 1000 kilos. of uranium. Since then further measurements, carried out by Miss Hitchens last year, have shown definitely for the first time a clear growth of radium from uranium in the largest preparation, containing 3 kilos. of uranium, and this growth, as theory requires, is proceeding according to the square of the time. In three years it amounted to 2×10^{-11} grams of radium, and in six years to just four times this quantity. From this result it was concluded that the previous estimate of 100,000 years for the period of ionium, though still of the nature of a minimum rather than a maximum, was very near to the actual period.

Joachimsthal pitchblende, the Austrian source of radium, contains only an infinitesimal proportion of thorium. An ionium preparation separated, by Auer von Welsbach, from 30 tons of this mineral, since no thorium was added during the process, was an extremely concentrated ionium preparation. The atomic weight of ionium—calculated by adding to the atomic weight of its product, radium, four for the α -particle expelled in the change—is 230, whereas that of thorium, its isotope, is slightly above 232. The question was whether the ionium-thorium preparation would contain enough ionium to show the difference. Hönigschmid and Mlle. Horovitz have made a special examination of the point, first redetermining as accurately as possible the atomic weight of thorium and then that of the thorium-ionium preparation from pitchblende. They found 232.12 for the atomic weight of thorium, and by the same method 231.51 for that of the ionium-thorium. A very careful and complete examination of the spectra of the two materials showed for both absolutely the same spectrum and a complete absence of impurities.

If the atomic weight of ionium is 230, the ionium-thorium preparation must, from its atomic weight, contain 30 per cent of ionium and 70 per cent of thorium by weight. Professor Meyer has made a comparison of the number of α -particles given per second by this preparation with that given by pure radium, and found it to be in the ratio of 1 to 200. If 30 per cent is ionium, the activity of pure ionium would be one-sixtieth of that of pure radium, its period some sixty times greater, or 150,000 years. This confirms in a very satisfactory manner our direct estimate of 100,000 years as a minimum, and incidentally raises rather an interesting question.

My direct estimate involves directly the period of uranium itself, and if the value accepted for this is too high, that for the ionium will be correspondingly too low. Now, last week, Professor Joly was

bringing before you, I believe, some of his exceedingly interesting work on pleochroic halos, from which he has grounds for the conclusion that the accepted period of uranium may be too long. But since I obtained, for the period of ionium, a minimum value two-thirds of that estimated by Meyer from the atomic weight, it is difficult to believe that the accepted period of uranium can have been overestimated by more than 50 per cent of the real period. The matter could be pushed to a further conclusion if it were found possible to estimate the percentage of thorium in the thorium-ionium preparation, a piece of work that ought not to be beyond the resources of radio-chemical analysis. This would then constitute a check on the period of uranium as well as on that of ionium. Such a direct check would be of considerable importance in the determination of geological ages.

The period of ionium enables us to calculate the ratio, between the weights of ionium and uranium in pitchblende, as 17.4 to 10^1 , and the doctrine of the non-separability of isotopes leads directly to the ratio, between the thorium and uranium in the mineral, as 41.7 to 10^9 . This quantity of thorium is, unfortunately, too small for direct estimation. Otherwise it would be possible to devise a very strict test of the degree of non-separability. As it is, the work is sufficiently convincing. Thirty tons of a mineral containing a majority of the known elements in detectable amount, in the hands of one whose researches in the most difficult field of chemical separation are world-renowned, yield a preparation of the order of one-millionth of the weight of the mineral, which cannot be distinguished from pure thorium in its chemical character. Anyone could tell in the dark that it was not pure thorium, for its α -activity is 30,000 times greater than that of thorium. This is then submitted to that particular series of purifications designed to give the purest possible thorium for an atomic weight determination, and it emerges without any separation of the ionium, but with a spectrum identical with that of a control specimen of thorium similarly purified. The complete absence of impurities in the spectrum show that the chemical work has been very effectively done, and the atomic weight shows that it must contain 30 per cent by weight of the isotope ionium, a result which agrees with its α -activity and the now known period of the latter.

DETERMINATION OF ATOMIC WEIGHTS.

The results enumerated thus prove that the atomic weight can no longer be regarded as a natural constant, or the chemically pure element as a homogeneous type of matter. The latter may be, and doubtless often is, a mixture of isotopes varying in atomic weight over a small number of units, and the former then has no exact physical significance, being a mean value in which the proportions of

the mixture as well as the separate atomic weights are both unknown. New ideals emerge and old ones are resuscitated by this development. There may be after all a very simple numerical relation between the true atomic weights. The view that seems most probably true at present is that while hydrogen and helium may be the ultimate constituents of matter in the Proutian sense, and the atomic weights therefore approximate multiples of that of hydrogen, small deviations, such as exist between the atomic weights of these two constituent elements themselves, may be due to the manner in which the atom is constituted, in accordance with the principle of mutual electro-magnetic mass, developed by Silberstein and others. The electro-magnetic mass of two charges in juxtaposition would not be the exact sum of the masses when the charges are separated. The atomic weight of hydrogen is 1.0078 in terms of that of helium as 3.99, and that the latter is not exactly four times the former may be the expression of this effect. Harkins and Wilson have recently gone into the question with some thoroughness, and the conclusion of most interest in the present connection, which appears to emerge, is in favour of regarding most of the effect to occur in the formation of helium from hydrogen, and very little in subsequent aggregations of the helium. In the region of the radio-elements, where we have abundant examples of the expulsion of helium atoms as α -particles, it seems as if we could almost safely neglect this effect altogether. Thus radium has the atomic weight almost exactly 226, and the ultimate product almost exactly 206, showing that in 5 α - and 4 β -ray changes the mean effect is nil, and the atomic weights are moreover integers in terms of oxygen as 16, or helium 4. It is true that the atomic weights of both thorium and uranium are between 0.1 and 0.2 greater than exact integers, but it is difficult to be sure that this difference is real.

When, among the light elements, we come across a clear case of large departure from the integral value, such as magnesium 24.32 and chlorine 35.46, we may reasonably suspect the elements to be a mixture of isotopes. If this is true for chlorine, it suggests a most undesirable feature in the modern practice of determining atomic weights. More and more the one method has come to be relied upon: the preparation of the chloride of the element and the comparison of its weight with that of the silver necessary to combine with the chlorine, and with the weight of the silver chloride formed.

Almost the only practical method, and that a very laborious and imperfect one, which may be expected to resolve a mixture of isotopes, is by long-continued fractional gaseous diffusion, which is likely to be the more effective the lower the atomic weight. Assume, for example, chlorine were a mixture of isotopes of separate atomic weights 34 and 36, or 35 and 36. The 34 isotope would diffuse some 3 per cent faster than the 36, and the 35 some 1.5 per cent faster.

The determination of the atomic weight of chlorine in terms of that of silver has reached now such a pitch of refinement that it should be able to detect a difference in the end fractions of the atomic weight of chlorine, if chlorine or hydrogen chloride were systematically subjected to diffusion. It is extremely desirable that such a test of the homogeneity of this gas should be made in this way.

Clearly a change must come in this class of work. It is not of much use starting with stuff out of a bottle labelled "purissimum" or "garantirt," and in determining to the highest possible degree of accuracy the atomic weight of an element of unknown origin. The great pioneers in the subject, like Berzelius, were masters of the whole domain of inorganic chemistry, and knew the sources of the elements in Nature first-hand. Their successors must revert to their practice and go direct to Nature for their materials, must select them carefully with due regard to what geology teaches as to their age and history, and, before carrying out a single determination, they must analyse their actual raw materials completely, and know exactly what it is they are dealing with. Much of the work on the atomic weight of lead from mixed minerals is useless, for failure to do this. They must rely more on the agreement, or disagreement, of a great variety of results by methods as different and for materials as different as possible, rather than on the result of a single method pushed to the limit of refinement, for an element provisionally purified by a dealer from quite unknown materials. The preconceived notion, that the results must necessarily agree if the work is well done, must be replaced by a system of co-operation between the workers of the world checking each other's results for the same material. A year ago anyone bold enough to publish atomic weight determinations, which were not up to the modern standards of agreement among themselves, would have been regarded as having mistaken his vocation. If these wider ideals are pursued, all the labour that has been lavished in this field, and which now seems to have been so largely wasted, may possibly bear fruit, and where the newer methods fail, far below the narrow belt of elements which it is possible to watch changing, the atomic weight worker may be able to pick up the threads of the great story. No doubt it is writ in full in the natural records preserved by rock and mineral, and the evidence of the atomic weights may be able to carry to a triumphant conclusion the course of elementary evolution, of which as yet only an isolated chapter has been deciphered.

THE STRUCTURE OF THE ATOM.

The third line of recent advance, which does much to explain the meaning of the isotopes and the Periodic Law, starts from Sir Ernest Rutherford's nuclear theory of the atom, which is an attempt to determine the nature of atomic structure, which again is

the necessary preliminary to the understanding of the third aspect in which the elements are or may be complex. That uranium and thorium are built up of different isotopes of lead, helium and electrons is now an experimental fact, since they have been proved to change into these constituents. But the questions how they are built up, and what is the nature of the non-radioactive elements, which do not undergo changes, remain unsolved.

Professor Bragg showed in 1905 that the α -particles can traverse the atoms of matter in their path almost as though they were not there. As far as he could tell, and the statement is still true of the vast majority of α -particles colliding with the atoms of matter, the α -particle ploughs its way straight through, pursuing a practically rectilinear course, losing slightly in kinetic energy at each encounter with an atom, until its velocity is reduced to the point at which it can no longer be detected. From that time, the α -particle became as it were, a messenger that could penetrate the atom, traverse regions which hitherto had been bolted and barred from human curiosity, and on re-emerging could be questioned, as it was questioned, effectively by Rutherford, with regard to what was inside. Sir J. J. Thomson, using the electron as the messenger, had obtained valuable information as to the number of electrons in the atom, but the massive material α -particle alone can disclose the material atom. It was found that, though the vast majority of α -particles re-emerge, from their encounters with the atoms, practically in the same direction as they started, suffering only slight hither and thither scattering due to their collisions with the electrons in the atom, a minute proportion of them suffer very large and abrupt changes of direction. Some are swung round, emerging in the opposite to their original direction. The vast majority, that get through all but undeflected, have met nothing in their passage save electrons, 8000 times lighter than themselves. The few, that are violently swung out of their course, must have been in collision with an exceedingly massive nucleus in the atom, occupying only an insignificant fraction of its total volume. The atomic volume is the total volume swept out by systems of electrons in orbits of revolution round the nucleus, and beyond these rings or shells guarding the nucleus it is ordinarily impossible to penetrate. The nucleus is regarded by Rutherford as carrying a single concentrated positive charge, equal and opposite to that of the sum of the electrons.

Chemical phenomena deal almost certainly with the outermost system of detachable or valency electrons alone, the loss or gain of which conditions chemical combining power. Light spectra originate probably in the same region, though possibly more systems of electrons than the outermost may contribute, while the X-rays and γ -rays seem to take their rise in a deep-seated ring or shell around the nucleus. But mass phenomena, all but an insignificant fraction, originate in the nucleus.

In the original electrical theory of matter, the whole mass of the atom was attributed to electrons, of which there would have been required nearly 2000 times the atomic weight in terms of hydrogen as unity. With the more definite determination of this number, and the realisation that there were only about half as many as the number representing the atomic weight, it was clear that all but an insignificant fraction of the mass of the atom was accounted for. In the nuclear hypothesis this mass is concentrated in the exceedingly minute nucleus. The electro-magnetic theory of inertia accounts for the greater mass if the positive charges that make up the nucleus are very much more concentrated than the negative charges which constitute the separate electrons. The experiments on scattering clearly indicated the existence of such a concentrated central positive charge or nucleus.

The mathematical consideration of the results of α -ray scattering, obtained for a large number of different elements, and for different velocities of α -ray, gave further evidence that the number of electrons, and therefore the + charge on the nucleus, is about half the number representing the atomic weight. But van der Broek, reviving an isolated suggestion from a former paper full of suggestions on the Periodic Law, which were, I think, in every other respect at fault, suggested that closer agreement with the theory would be obtained if the number of electrons in the atom, or the nuclear charge, was the number of the place the element occupied in the Periodic Table. This is now called the atomic number, that of hydrogen being taken as 1, helium 2, lithium 3, and so on to the end of the table, uranium 92, as we now know. For the light elements, it is practically half the atomic weight; for the heavy elements, rather less than half.

I pointed out this accorded well with the law of radioactive change that had been established to hold over the last thirteen places in the Periodic Table. This law might be expressed as follows: The expulsion of the α -particle carrying two positive charges lowers the atomic number by two, while the expulsion of the β -particle, carrying a single negative charge, increases it by one. In ignorance of van der Broek's original suggestion, I had, in representing the generalisation, shown the last thirteen places as differing by unit by unit in the number of electrons in the atom.

Then followed Moseley's all-embracing advance, showing how from the wave-lengths of the X-rays, characteristic of the elements, this conception explained the whole Periodic Table. The square roots of the frequency of the characteristic X-rays are proportional to the atomic numbers. The total number of elements existing between uranium and hydrogen could thus be determined, and it was found to be ninety-two, only five of the places being vacant. The "exceptions" to the Periodic Law, such as argon and potassium, nickel and cobalt, tellurium and iodine, in which an element with higher atomic weight precedes instead of succeeds one with lower, was confirmed by the

determination of the atomic numbers in every case. From now on, this number, which represents the + charge on the nucleus, rather than the atomic weight, becomes the natural constant which determines chemical character, light and X-ray spectra, and, in fact, all the properties of matter, except those that depend directly on the nucleus—mass and weight on the one hand, and radioactive properties on the other.

What, then, were the isotopes on this scheme? Obviously they were elements with the same atomic number, the same *nett* charge on the nucleus, but with a differently constituted nucleus. Take the very ordinary sequence in the disintegration series, one α - and two β -rays being successively expelled in any order. Two + and two - charges have been expelled, the *nett* charge of the nucleus remains the same, the chemical character and spectrum the same as that of the first parent, but the mass is reduced 4 units because a helium atom, or rather nucleus, has been expelled as an α -particle. The mass depends on the *gross* number of + charges in the nucleus, chemical properties on the difference between the gross numbers of + and - charges. But the radioactive properties depend not only on the *gross* number of charges but on the constitution of the nucleus. We can have isotopes with identity of atomic weight, as well as of chemical character, which are different in their stability and mode of breaking up. Hence we can infer that this finer degree of isotopy may also exist among the stable elements, in which case it would be completely beyond our present means to detect. But when transmutation becomes possible such a difference would be at once revealed.

The case is not one entirely of academic interest, because it is probable that the reconciliation of the conflicting views of the geologists and chemists, who concluded that lead was not the ultimate product of thorium, and those who by atomic weight demonstrations on the lead have shown that it is, depends probably on this point.

As has long been known, thorium-C, an isotope of bismuth, disintegrates dually. For 35 per cent of the atoms disintegrating, an α -ray is expelled followed by a β -ray. For the remaining 65 per cent the β -ray is first expelled and is followed by the α -ray. The two products are both isotopes of lead, and both have the same atomic weight, but they are not the same. More energy is expelled in the changes of the 65 per cent fraction than in those of the 35 per cent. Unless they are both completely stable a difference of period or change is to be anticipated.

The same thing is true for radium-C', but here all but a very minute proportion of the atoms disintegrating follow the mode followed by the 65 per cent in the case of thorium-C'. The product in this case, radium-D, which, of course, is also an isotope of lead, with atomic weight 210, is *not* permanently stable, though it has a fairly long period, 24 years. The other product is not known to change

further, but then, even if it did, it is in such small quantity that it is doubtful whether the change would have been detected. But, so far as is known, it forms a stable isotope of lead of atomic weight 210, formed in the proportion of only 0.03 per cent of the whole.

Now the atomic weight evidence merely shows that *one* of the two isotopes of lead formed from thorium is stable enough to accumulate over geological epochs, and it does not necessarily follow that both are. Dr. Arthur Holmes has pointed out to me that the analysis I gave of the Ceylon thorite leads to a curiously anomalous value for the age of the mineral. The quantity of thorium lead per gram of thorium is 0.0062, and this, divided by the rate at which the lead is being produced, 4.72×10^{11} gram of lead per gram of thorium per year, gives the age as 131 million years. But a Ceylon pitchblende, with uranium 72.88 per cent and lead 1.65 per cent, and ratio of lead to uranium as 0.064, gives the age as 512 million years. Dr. Holmes regards the two minerals as likely to be of the same age, and the pitchblende to be, of all the Ceylon results, the one most trustworthy for age measurement.

If we suppose that, as in the case of radium-D, the 65 per cent isotope of lead derived from thorium is *not* stable, and that only the 35 per cent isotope accumulates, the age of the mineral would be 375 million years, which the geologists are likely to consider much more nearly the truth. But the most interesting point is that, if we take the atomic weight of the lead isotope derived from uranium as 206.0, and that derived from thorium as 208.0, and calculate the atomic weight of the lead in Ceylon thorite, assuming it to consist entirely of uranium lead and of only the 35 per cent isotope from thorium, we get the value 207.74, which is exactly what I found from the density, and what Prof. Hönigschmid determined (207.77).

The question remains, if this is what occurs, what does this unstable lead change into? If an α -particle were expelled mercury would result, or if a β -particle bismuth, two elements of which I could find no trace in the lead group separated from the whole 20 kilos. of mineral. But if an α - and a β -particle were both expelled, the product would be thallium, which is present in amount small but sufficient for chemical as well as spectroscopic characterisation. If the process of disintegration does proceed as suggested, it should be possible to trace it, for this particular lead should give a feeble specific α - or β -radiation, in addition, of course, to that due to other lead isotopes. So far it has not been possible to test this. In the meantime, the explanation offered is put forward provisionally as being consistent with all the known evidence.

Looking for a moment in conclusion at the broader aspects of the new ideas of atomic structure, it seems that though a sound basis for further development has been roughed out, almost all the detail remains to be supplied. We have got to know the nucleus, but beyond the fact that it is constituted, in heavy atoms, of nuclei of

helium and electrons, nothing is known. Whilst as regards the separate shells or rings of electrons which neutralise its charge and are supposed to surround it, like the shells of an onion, we really know nothing yet at all. The original explanation, in terms of the electron, of the periodicity of properties displayed by the elements, still remains all that has been attempted. We may suppose, as we pass through the successive elements in the table, one more electron is added to the outermost ring for each unit increase in the charge on the nucleus, or atomic number, and that when a certain number, 8 in the early part of the table, 18 later, a complete new stable shell or ring forms, which no longer participates directly in the chemical activities of the atom. Thanks, however, to Moseley's work, this now is not sufficiently precise; for we know the exact number of the elements, and the various atomic numbers at which the remarkable changes, in the nature of the periodicity displayed, occur. Any real knowledge in this field will account not only for the two short initial periods, but also for the curious double periodicity later on, in which the abrupt changes of properties in the neighbourhood of the zero family alternate with the gradual changes in the neighbourhood of the VIIIth groups. The extraordinary exception to the principle of the whole scheme presented by the rare-earth elements remains a complete enigma, none the less impressive because, beyond them again in the table, the normal course is resumed and continues to the end.

[F. S.]

Friday, January 18, 1918.

HIS GRACE THE DUKE OF NORTHUMBERLAND, P.C. K.G.
LL.D. F.R.S., President, in the Chair.

PROFESSOR SIR JAMES DEWAR, M.A. LL.D. D.Sc. F.R.S. M.R.I.,
Fullerian Professor of Chemistry.

Studies on Liquid Films.

SOME problems presented by liquid films were discussed in the Discourse of 1917.* These studies have been continued and further developed in the restricted time left for research after meeting the demands of Government Departments ; but such conditions imply a certain amount of discontinuity which cannot but leave its mark on the inquiry.

BUBBLES FOUR FEET IN DIAMETER.

In order to increase the size of bubbles above those described a year ago (46 cm. in diameter), advantage was taken of a cool cement-lined cellar (some 600 cubic feet capacity) which was so fitted that the nozzle and blowing tube were passed through the door and controlled from outside. All apertures and cracks were filled with glycerined cotton wool. The atmosphere of the cellar was several times cleaned and renewed by pumping in purified air, but no permanent purity could be maintained. In less than two days the Tyndall cone would reappear. Large sheets and trays smeared with glycerin were of no assistance in reducing the mist, so that although bubbles up to four feet in diameter were obtained, they did not last above a few hours.

PLANE BLACK FILMS 2500 Sq. CM. IN AREA.

At the Discourse given a year ago a stoppered vessel was shown which contained a plane black film 19 cm. in diameter ; the film was then one week old, and has remained unchanged to this date.

* "Soap Bubbles of Long Duration," Proc. Roy. Inst., Vol. XXII. p. 179.

For the purpose of extending the study to larger films, the cylindrical globes that were used last year for the examination of 40 cm. bubbles were employed. Plane films $56\frac{1}{2}$ cm., or nearly two feet in diameter, were thereby obtained which lasted for 40 days, and even more, after becoming entirely black. Fig. 1 shows a globe fitted for this purpose. About half a litre of soap solution having been run in, and the end of the tube A dipped into it, a bubble, blown by pure air, was started and gradually expanded, as shown by the various stages of the diagram, until it became a plane horizontal film about the middle of the vessel. Some idea of the appearance of the film in the globe can be gathered from Fig. 2, reproduced from a photograph taken with a white screen placed behind and a little above the film, thus reflecting diffused light.

The globe and its fittings must be scrupulously clean, and the interior free from all traces of floating matter when tested by the Tyndall cone of light. By careful manipulation the soap solution was made to flow all over the inside, while the tube A was also wetted by a stream of soap solution from a dropping funnel F fitting tightly in the rubber cork used to close the neck of the globe. The tube A can slide freely up and down in the support tube B, to which was sealed the bulbed outlet E. The upper part of A could, on occasion, be fitted with a dropping funnel C, sealed to the vertical portion, while still connected to the bulbed nozzle D, by which pure air was admitted. The bulbs D, E were loosely packed with cotton wool moistened with glycerin. C was only used when subsequent additions had to be made to the soap solution in the globe.

After the plane film was obtained in the right position midway in the globe, A was raised until its lower end was a few inches below the film. The nozzles D and E were open, but were provided with soda-lime guard tubes, so that the spaces above and below the film were equally open to the atmosphere, though guarded from contamination. This ensured that the fluctuations of the atmosphere were equalised throughout both portions of the relatively large space of the globe; otherwise the film was not likely to last long because of the vertical displacements that would occur. In one case a barometric alteration of 1 cm. in 20 hours caused the film to move through 5 mm. After the globe has drained for a day or two, there is not enough liquid left on the walls to keep the film sufficiently lubricated to allow of such oscillations. The only liquid available is in the tiny channel—the Gibbs layer—round the periphery of the film. This channel is roughly triangular in section, with the base of the triangle on the glass walls, and the concave sides converging to the film which extends out beyond the apex of the triangle. In a very well-drained film the base of this triangle may not be more than 0.1 mm., so that the sectional area of the channel is about $\frac{1}{20000}$ th of a sq. cm. The total liquid available round such a film 56 cm. diameter is, therefore, only about 1 cgm. It is obvious that

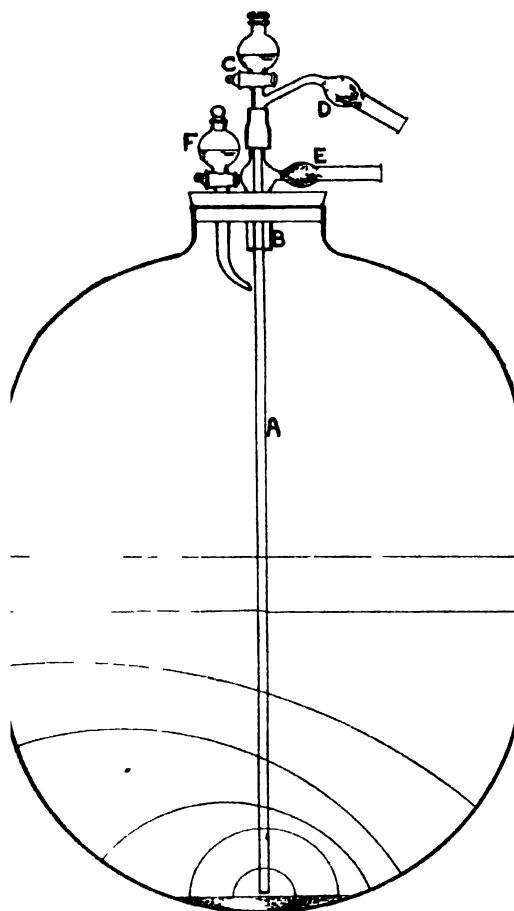


FIG. 1

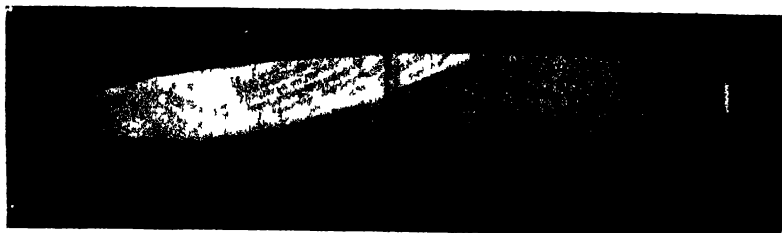


FIG. 2.

long before such complete drainage as this is reached any movement of the film occurring over a relatively dry surface will quickly exhaust the liquid in the channel, and the film will be ruptured. However, when the proper precautions were taken, the displacements due to atmospheric variations did not amount to more than 1 or 2 mm. for weeks together.

Until they become completely black very striking colour effects can be seen in these large horizontal films. They have of course only a small gradient of thickness, so that the bands of colour are drawn out into large areas. During this period convection in the films is most easily seen, because of the brilliant contrasts afforded by the moving portions. Should there be much fluctuation of temperature, the complete development to the black state may be arrested, the last part of the coloured area being kept in intermittent circulation for several days. Superfluous liquid draining down outside the central tube will produce a similar result by becoming spread out on the black film surface as a coloured clot round the tube. When this clot grows sufficiently it will draw off slowly, and pass down the radius of greatest inclination of the film. It formed on one occasion an ellipse (1 cm. by $1\frac{1}{2}$ cm.) which took 35 seconds to traverse the last one-fourth of its path. On approaching the periphery where the film curves up slightly into contact with the glass, the clot flattened out and curled into the most intricate convolutions, finally sweeping round close to the edge, a writhing mass of coloured streaks, many of which became roving stars on the black film. The whole coloured area was finally drawn into the Gibbs ring, from which frequent escapes of small drops of liquid took place.

A favourable condition for longevity is a quiet temperature rather below 10°C . Sudden alterations of 3 or 4°C . are most likely to burst the films by provoking too rapid convection therein, as is evidenced by very rapidly moving streams of silvery stars drawn from the Gibbs ring.

The vibrations which occurred during the operation of the air compressors in the Laboratory did not affect the final stability of the black films. A stationary circular wave was produced having an amplitude of over 1 mm. vertically all round a circle midway between the central tube and the walls of the globe. This motion continued the whole time the machines were working, but the films always survived.

Instead of having one large plane black film, a mesh-work of black films can be obtained completely filling the globe. To produce this, the lower end of the blowing tube A (Fig. 1) is inserted slightly below the surface of the soap solution. The air current being regulated suitably to the diameter of the tube A, a steady succession of uniform bubbles is produced. The surface of the glass having previously been well moistened, the issuing bubbles conse-

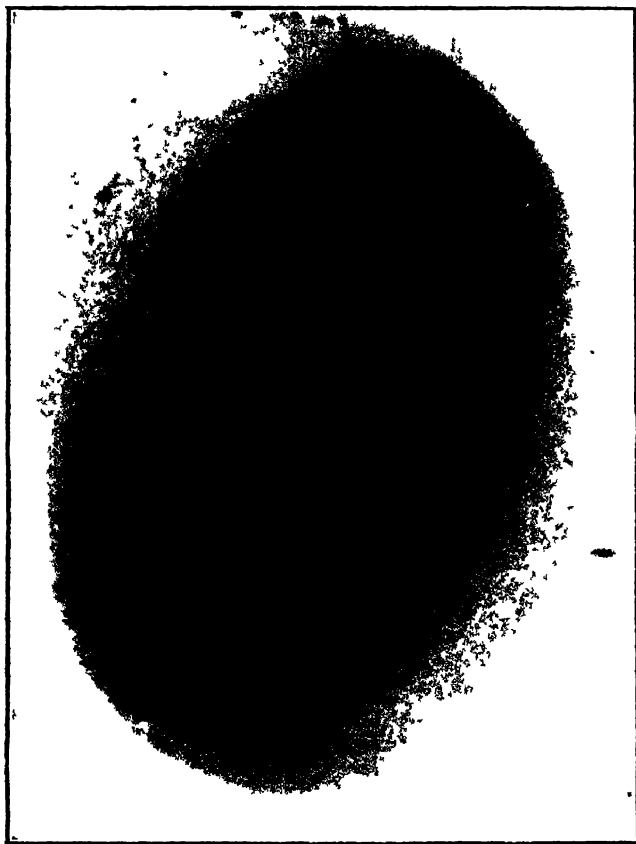


FIG. 3a.



FIG 3b

quently encounter little resistance, and develope rapidly, linking up into a glittering lustrous froth which increases until the globe is full. Excess liquid drains away very rapidly, the black stage being reached in about an hour. The beauty of the mass can be seen properly only when a beam of light is flashed upon it in continually changing directions, the different inclinations of the internal plane films giving rise to a continuous series of brilliant scintillations (Fig. 3*a*). The same appearance is perhaps still more remarkable when the mesh-work is lit up by diffused light from rays thrown across the observer's line of vision (Fig. 3*b*). A black background is used in both cases.

The internal walls of the various cells being plane polygons, the pressure of the air in these cells is the same for all, and is regulated according to the curvature of the cell-walls on the outer boundary. As transference of the enmeshed air from the mass can take place only through the curved boundaries of the outer layer of bubbles, contraction of the mass from this cause is relatively slow. In one case it required a fortnight for the initial volume to be reduced to one half.

To obtain the best result the blowing tube A should be withdrawn when the mesh-work has been completed, as it exerts some protecting power over the bubbles that closely surround it, thus causing an annular depression farther out, and tending to destroy the mass.

COLUMNS AND CHAINS OF BUBBLES.

For the purpose of studying bubble clusters and film complexes, instead of single bubbles and plane films, an arrangement of the nozzle was employed, by which it was possible to get a succession of bubbles of any required volume, linked together, in one operation. The apparatus employed is shown in Fig. 4. A is a stoppered reservoir of soap solution from which a capillary tube passes down the air-supply tube D, B, to about 1 cm. above a constriction K. After passing K the lower end of the air-supply tube is, for convenience, fitted by a ground joint to an enlarged nozzle C, securely held in position by the rubber cork E. The stopper A being opened at regulated intervals of time, a series of drops falls on the constriction K, which are immediately blown into films by the constant air current entering through the bulb D (protected as before by lightly packed glycerined cotton wool). Hence a series of bubbles is produced at the nozzle C,

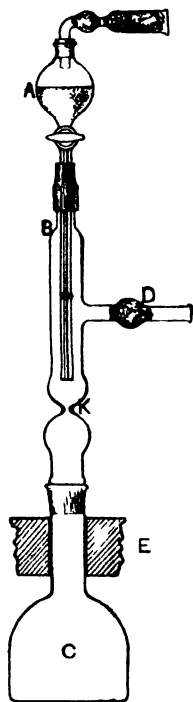


FIG. 4.

which may have equal or different volumes as desired, and may be further controlled so as to present themselves either as a vertical column or as a cluster.

The shape of the cluster obtained depends on the dimensions of the nozzle, the speed of the air current, and the relation between the mass of the drop and the size of the constriction. If the drop be too large or the air current too slow, extra films result from the accumulation of superfluous liquid; the same thing happens with an elongated constriction. On the other hand, too rapid a current may simply spray the liquid over the interior of the nozzle. The cleanest working is obtained from a short neck blown out above and below in a spherical shape as shown in the figure at K.

A succession of equal bubbles may either form a regular cluster on the mouth of the nozzle, or a vertical chain or column of spherical segments united by plane circular films. A cluster will usually be formed when the bubbles are less in diameter than the nozzle, and a chain or column when the bubbles are larger. For the manipulation of these complexes an air-tight, cubical, plate-glass chamber was made (Fig. 5), on a frame of aluminium alloy (edge, 50 cm.). The glass plate for the top was 1 cm. thick; holes were cut in it for the rubber corks that held the nozzles and supported the movable glass rods which carried the different small pieces of apparatus used to catch and control the chains while being formed.

For the manipulation of the longer columns the glass cylinder shown in Fig. 6 was used. It was 3 feet long and 6 inches in diameter; its ends made air-tight joints with two plates, the upper of which held the blowing nozzle, while the lower held a support ring. Suitable exit stopcock and soda-lime guard tube were also fitted. The support ring was sealed to the top of a vertical rod that could slide up and down in an air-tight joint in the bottom plate. The cylinder was fixed on a shelf in the middle of a massive wooden stand, and a hole was cut in the shelf to allow free movement to the sliding rod. When a to-and-fro motion was given to the support rod, the flexibility of the column was readily seen; transverse waves appeared to pass up the whole length, each segment moving on the one adjacent as if attached by a very free universal joint. By drawing the rod down a considerable extension could be obtained; contrariwise by raising it a bulging or spiral formation would result. If this be carried further and the surface be sufficiently moist, the column will sag out into contact with the glass walls and form a chain of oval segments. In a wider vessel, however, the segments can in this way be linked up successively to form regular clusters.

A beautiful exhibition of multiple scintillating coloured reflections is obtained when a beam from an arc lamp below is directed up through the column while the support rod is moved. An even more complete illumination is secured by using a white lined hood above, in which is hidden a 200-watt lamp, with two white wings of stiff

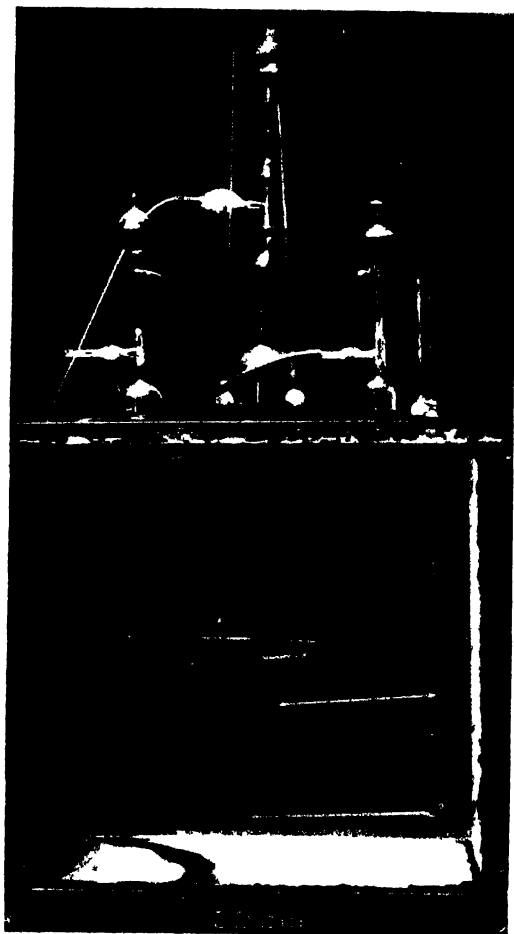


FIG. 5.

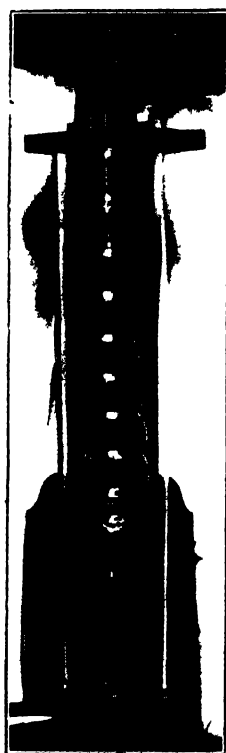


FIG. 6.

card fixed one on each side of the central black stand. These side screens alone are sufficient for this purpose if the whole apparatus stands in a good light. A striking contrast is obtained when the column is drained to blackness and illuminated by a beam from below, if an occasional drop of soap solution is allowed to trickle down through the nozzle. Before this is done very little is seen except the bright point reflections from the curved surfaces; but, as the falling drops arrive in rapid succession at the planes between the adjacent segments, the thin circular channels flash up into sparkling silvery light from the internal reflections of the accumulated liquid. Fig. 7 gives some idea of the appearance.

The following particulars show how some of the results were obtained :—

(a) Nozzle, 3 cm. diameter; constriction, 1.15 mm. bore; drop, 18 mgms.; air current approximately 500 c.c. a minute; drop interval, 5 seconds; giving a volume of 42 c.c. for each segment. While they were being blown the free end was caught on one of the movable glass rings already mentioned, by means of which fifteen bubbles were steadily drawn out into a flexible catenary with its ends 13 cm. apart (Fig. 8).

(b) Nozzle, 3.4 cm. diameter; air current, 565 c.c. per minute; drop interval, $7\frac{1}{2}$ seconds; giving a volume of about 70 c.c. for each segment. A column of eight of these bubbles reached from the rim of the nozzle to the wet floor of the cube, where contact was made. The same nozzle could give a chain of nine bubbles of three times this volume.

(c) Same nozzle; air current, 305 c.c. per minute; drop interval, $9\frac{1}{2}$ seconds; giving a volume of about 48 c.c. for each segment. A column of ten of these bubbles was held on a fairly straight axis inclined at about 50° to the horizontal after they were drained free of excess liquid.

Some of these chains are liable to break with excess liquid (Fig. 8). This can be largely obviated by using a percentage of hydrogen in the air current, provided an atmosphere of pure air is maintained in the glass cube. The buoyancy of the bubbles is thereby increased for a time sufficient to allow the column to be manipulated. When the chain has once been secured any further accumulation of liquid must be continually removed. For this purpose a fluted glass rod some 2 mm. thick and 3 or 4 cm. long was very effective. (It was made by drawing out a bundle of seven small glass rods in the blow-pipe, and was utilised by attachment to one of the movable bent glass rods passing through the top of the cubical box.)

When very large bubble segments are required it is safer to interrupt the air current between two adjacent segments, while a few extra drops of liquid are run in to remoisten the glass surfaces. In this way bubbles of over 1 litre were obtained on a nozzle 5 cm.

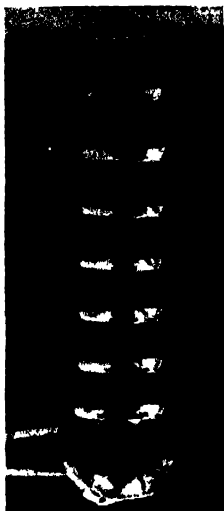


FIG.

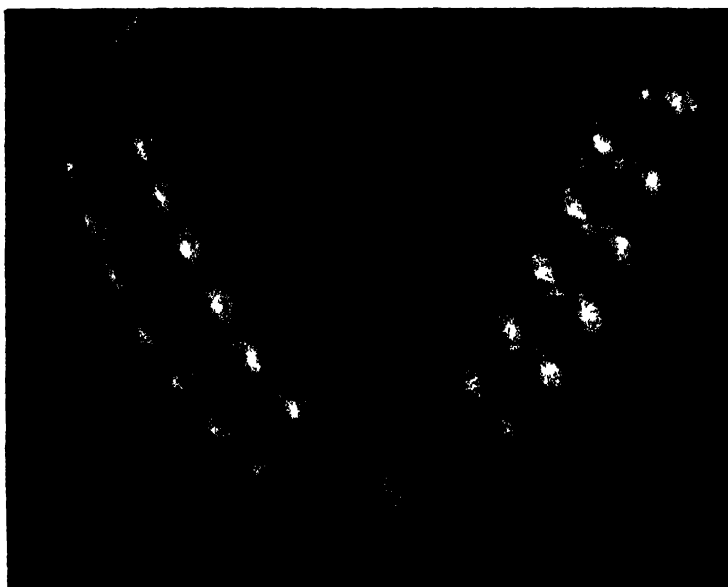


FIG. 8.

in diameter, with a constriction of 1 mm. bore, and a 25 mgm. drop. Four of these linked together and forming a chain inclined at about 45° to the vertical were photographed on a Lumière autochrome plate, which, in addition to the coloured contours, showed clearly the

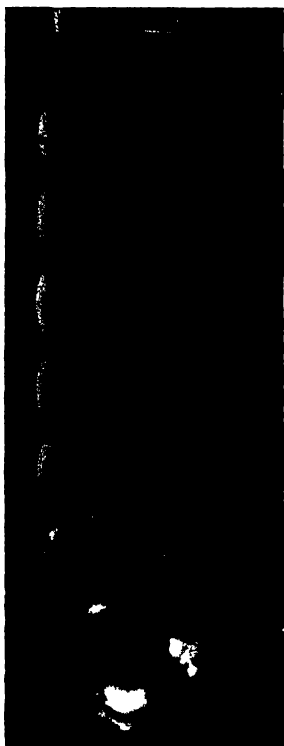


FIG. 9.



FIG 10.

brilliant bands on the plane films between the equal segments. To obtain these photographs the cubical glass vessel was placed in full sunlight. The top and two opposite sides were covered with thin tissue paper to give uniform diffuse illumination. Black paper formed the background, while the front was left clear for exposure

to the camera. On a quarter-plate an exposure of 40 to 60 seconds was necessary. A 9 by 7 inch Ross portrait lens was employed at F. 11. Colour photographs of several of the columns have been obtained in this way.

MULTIPLE COLUMNS.

Regular formations of greater complexity were obtained when the bubble elements were reduced in size so that their diameters were less than that of the nozzle. Thus, for example, two columns which coalesced into one are shown in two perpendicular views in

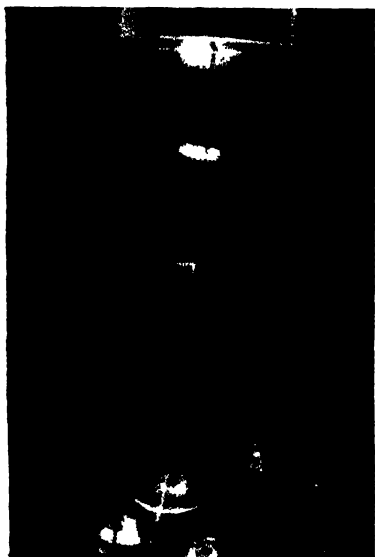


FIG. 11.



FIG. 12.

Figs. 9 and 10 (see also Fig. 24). The horizontal plane films between the successive elements of both columns were linked by a "staircase" of films, inclined right and left at 120° to the horizontal films; every bubble thus fitted into two bubbles of the adjacent half

column, the horizontal junction films being segments of circles, while the inclined films took the form of rectangles with their short sides slightly convex. The data for this formation were: Nozzle, 5 cm. diameter; air current, 130 c.c. per minute, with an interval of 15 seconds between successive drops. Each element of the column thus had a volume of $32\frac{1}{2}$ c.c.

Three columns will also coalesce from top to bottom, twining round each other like the spiral strands of a rope. The plane films linking the bubble segments are then truncated sectors of circles.

A complex of four interpenetrating vertical columns is shown in Figs. 11 and 12. This may be considered as built up by a succession of horizontal pairs of bubbles, each pair being at right angles to the adjacent pairs above and below. The symmetrical pairs of horizontal plane films which link them are circular quadrants with their points in contact, and of course are alternately at right angles.

Between each member of the alternate horizontal pairs of bubbles there are vertical films which are diamond-shaped, and joined at their apices with their planes alternately at right angles along the axis of the cluster. The resulting appearance is very regular. One example of this formation was produced by a nozzle of 5 cm. diameter, with an air current of 400 c.c. a minute, and an interval of 4 to 5 seconds between the drops.

A still more complex but perfectly regular quadruple column has the simple string of diamond-shaped films replaced by alternate hexagons and squares of which only the hexagons are vertical. An isometric view of this part of the arrangement is shown in Fig. 13. The common edges of adjacent squares and hexagons are horizontal, and alternate squares are equally inclined in opposite directions to the axis of the complex column. The complete configuration is shown in Figs. 14 and 15 (two perpendicular views); the outlines are further displayed in Fig. 16.

Multiple columns of a higher order were obtained by lessening the time-interval between the drops. The excess liquid thus supplied tended to distort the cluster. This was avoided by employing a long nozzle within which the network of bubbles was formed and supported until the excess liquid drained away. The cluster was then expanded clear of the nozzle, and remained stable and undistorted. As many as seven or more interlaced vertical columns were obtained in this manner. The centre bubbles of the cluster were of course completely enclosed, and hence had no curved surfaces, but formed instead a



FIG. 13.

chain of film-enclosed cells. From the outermost facets of these there radiated a film structure of pyramidal frustums bounded externally by curved bubble films. Two forms of these faceted "cells" are shown in Fig. 17; some have the regularity of a well-cut gem, and exhibit great brilliance in a concentrated light. Some forms frequently occurring have (a) parallel regular hexagons top and bottom with pentagonal facets; others have (b) irregular heptagons at the top and bottom; the facets being then either

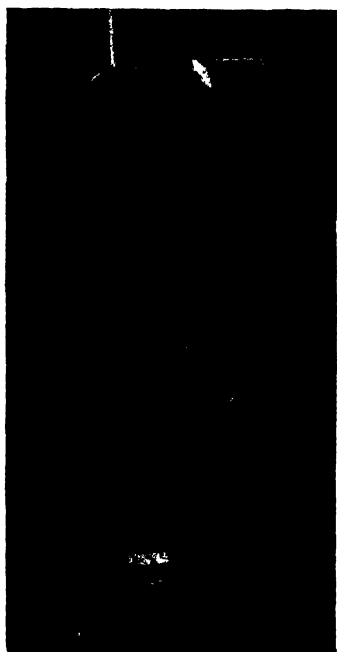


FIG. 14.



FIG. 15.

pentagons alone or alternate hexagons and quadrilaterals, or even all three together. An interesting example occurred when the quadruple column with alternate diamond-shaped planes distributed along the axis (Fig. 11) was disengaged from its nozzle and allowed to fall on the surface of the soap solution 15 cm. below. The cluster had already drained to complete blackness, and was therefore so light that at first it rebounded several cms., finally floating on the surface for some time, delicately poised like a nautilus.

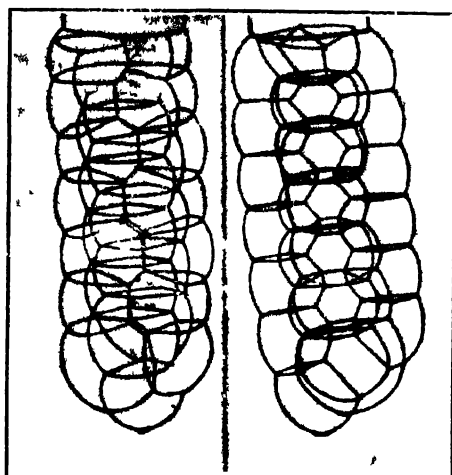


FIG 16

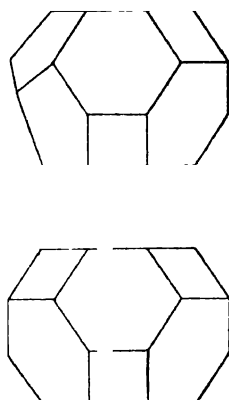
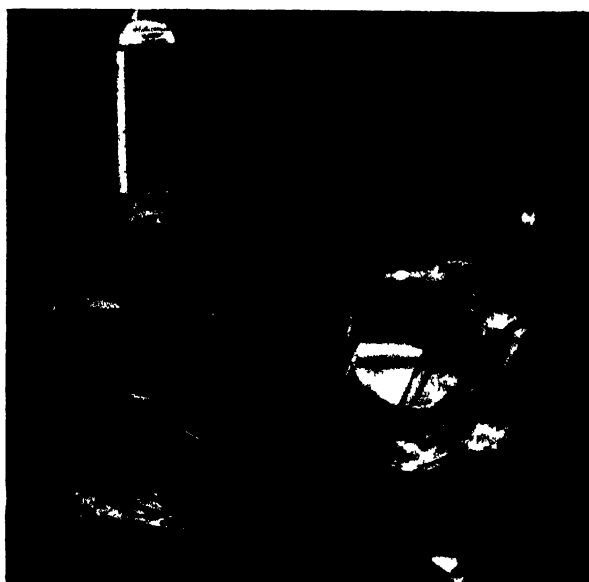


FIG 17.

(b)



(a)

FIG. 18.

However, it soon coalesced with the liquid surface, forming a half dodecahedron in the centre surrounded by a symmetrical ring of six half bubbles all resting on the liquid, and three whole bubbles superposed regularly above these, each of the nine external bubbles springing from one facet of the central "cell." The completed structure, of which this was the half, would thus have consisted of twelve pentagonal pyramidal frustums round a dodecahedron, the bases of the pyramids being the outer curved bubble surfaces. Such a complex was obtained separately, but it is difficult to show the configuration by means of a photograph.

SYMMETRICAL CLUSTERS OF BUBBLES.

Equal-sized bubbles are readily built up into well-defined groups that have many interesting properties. Their spherical contours, interlaced by a network of reflecting films, give them a graceful symmetry. Up to an aggregate of eight the growth is fairly simple. Each successive bubble springs instantaneously into its place with the appearance of being partly absorbed, though of course retaining its volume practically unchanged. Two bubbles thus coalesce into two spherical segments joined by a circular plane film. When a third bubble is introduced between these two the spherical boundaries are further reduced, and are spaced out between three equally inclined plane films, which are segments of circles in contact round the axis of symmetry.

With four bubbles there are two possible arrangements; the more stable form has the fourth bubble resting symmetrically on the group of three, so that the four segments are equally spaced on the frame of a regular tetrahedron. Six plane films in the shape of circle sectors are thus produced by the four segments coalescing round the centroid of the tetrahedron (Fig. 18*a*). But if the fourth bubble be introduced between any two of the three-group instead of at the junction of all three, then the form shown in Fig. 18*b* is obtained, which has a central plane film shaped like a rectangle with its short sides slightly curved, and two pairs of equally inclined planes springing from its long sides. These five planes constitute a frame linking the four bubble segments together.

In Fig. 19 these frames outlined in wire are shown as they appear (*a*) for the group of three; and (*b*), (*c*) for the two forms of the group of four; while Fig. 20 (outer set) gives the sections through the groups to show the inclination between the plane films, and the trace of the outer contours.

Only one arrangement of the five-group has been obtained. It is formed when two additional segments interpenetrate, one at each end of the axis of the three-group, the three upper plane films thus formed, meeting in one point of this axis, and the three lower plane films meeting in another point of the same axis.

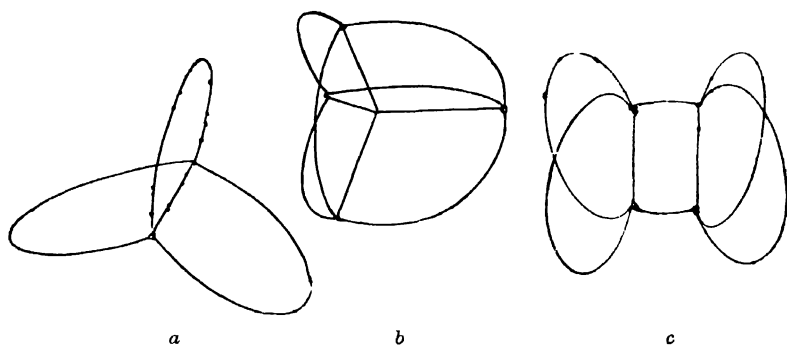


FIG. 19.

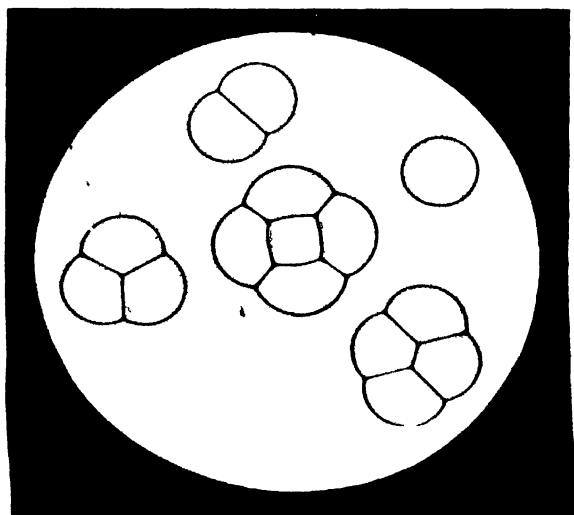


FIG. 20.



FIG. 21a



FIG. 21b

The groups of six, seven and eight all have the same type of symmetry—namely, at the centre is a small plane polygon, from the sides of which there radiates a ring of bubble segments, equally spaced, with two others on an axis at right-angles to the central plane. The six-group therefore has a ring of four segments round a square central plane, the two others being on opposite sides of this central plane. The two interlocked bubble segments thus take the form of two truncated square pyramids in contact with each other on the central square plane, having their bases bulged out on the spherical contour, and the four other segments built in round the

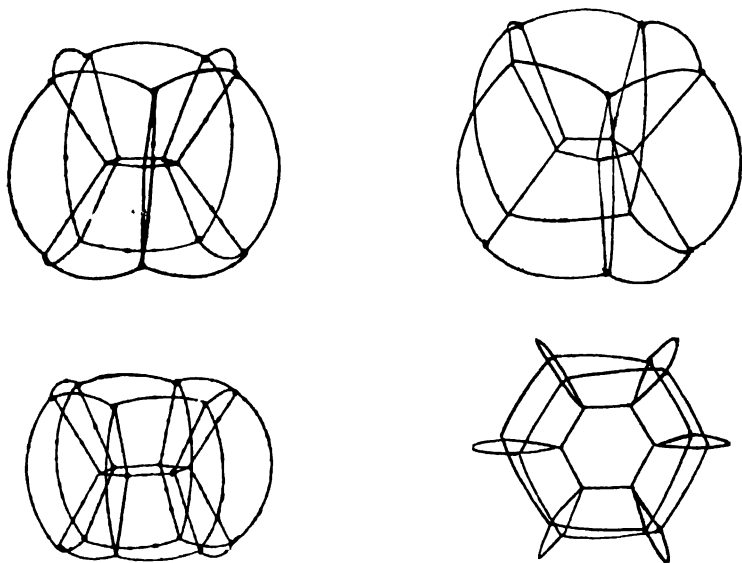


FIG. 22.

faces of the truncated pyramids (Fig. 21*a*). The section of this is shown in the central group of Fig. 20. The groups of seven and eight are similarly formed, except that the square central plane is replaced by a pentagon and hexagon respectively. In all cases the polygon edges are slightly curved. Fig. 21*b* is a photograph of the seven-group with pentagon centre. The wire frames for this group and the eight-group with hexagon centre are shown in Fig. 22, while sections through the two are given in Fig. 23.

These "sections" are in reality photographs of the half groups when formed on a horizontal glass plate (4 inches square). A fountain-pen filler was used to make the equal half bubbles, by

simply squeezing the indiarubber bulb quite flat, the nozzle having already been dipped in soap solution, and the glass plate well-moistened with solution. The single and double columns already described may be shown in the same simple manner (Fig. 24). By using the horizontal projection lantern these figures are plainly shown on the screen.

The forms taken by these clusters are governed by the conditions for equilibrium of the surface tensions at the intersections of the films. Not more than three films can meet in any one line, and if they are planes they will be equally inclined to one another at angles of 120° , while, if they are curved, then the law of equal inclinations holds between the tangent planes at all points of contact. Taking first the case of two bubbles which have coalesced into two segments united by a circular plane film, the tangent planes at any point of the line of contact of the curved surfaces will be inclined at 120° to each other and to the circular plane. It follows that the radius of the plane central film is $\frac{\sqrt[3]{3}}{2}$ of the radius of the two equal spherical

segments, the distance between their centres of curvature being equal to this radius, which is greater than the radius of the original separate bubbles in the ratio of $\sqrt[3]{4} : 1.5$ or $1.0 : 0.9452$. Therefore the internal excess pressure (which is inversely as the radius of curvature) is reduced 4.5 per cent. by the coalescence. Measurements made on two bubbles gave under 5 per cent.

Three spherical segments in contact are each approximately five-sevenths of a whole sphere. The internal pressures therefore are now reduced to the proportion of $\sqrt[3]{7} : \sqrt[3]{5}$ or $1 : 0.8933$. Now $0.8933 = (0.9452)^2$, so that the process appears to proceed by a geometrical progression, each linkage reducing the internal pressures in an equal proportion.

CONCENTRIC HALF BUBBLES.

An interesting application of the method of film formation by regulated drops was made in order to obtain a group of concentric hemispherical bubbles. It was desired to obtain them with a uniform difference of radii of 1 cm. between successive film surfaces. They were blown on the under side of the top glass plate of a smaller cubical vessel (30 cm. length of edge). A special form of nozzle was made with its rim flush with the surface on which the bubbles were to be blown. The part containing the narrow neck was of ebonite, and had a shoulder carefully fitted to the aperture in the glass plate. The dropping funnel and glass blowing tube were fitted tightly into the neck of the ebonite nozzle. Fig. 25 shows the arrangement with a group of ten half bubbles, the horizontal lines indicating the levels reached by black zones on the fourth day.

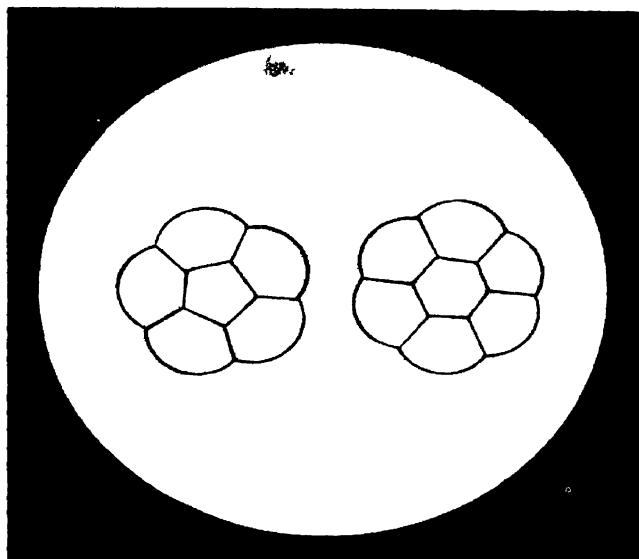


FIG 23

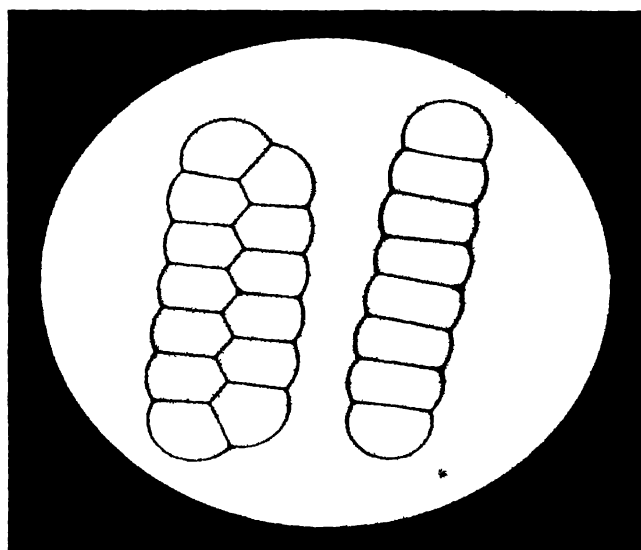


FIG 24

In order to determine the time at which each drop had to fall the volumes of the successive bubbles were calculated and their differences tabulated. Having fixed upon a suitable rate of blowing, the intervals between the drops that corresponded to the successive differences in volume were at once obtained. The rate of blowing was 216 c.c. per minute, so that the whole group took about 21 minutes to make, the intervals between the drops decreasing from about $4\frac{1}{2}$ minutes at first to about half a minute at the end. The surfaces of the glass plate and nozzle were first moistened with soap solution.

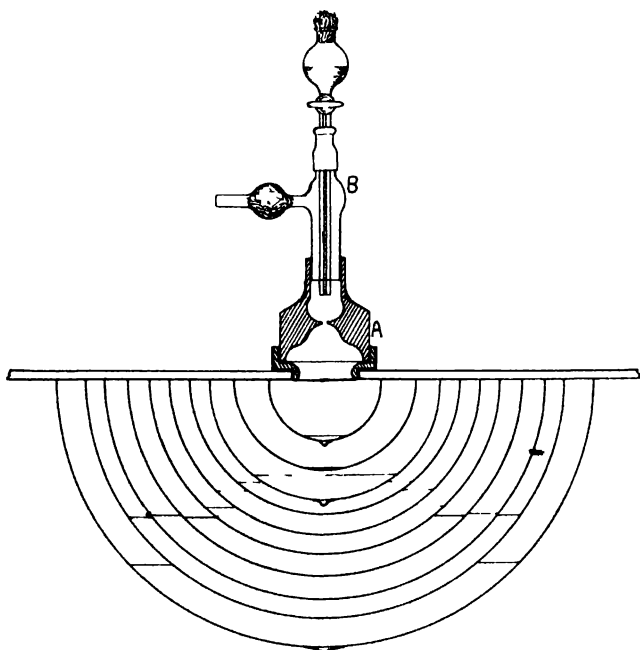


FIG. 25.

By the eighth day the black zones occupied 90 to 95 per cent. of the surfaces. Some experiments were made subsequently on the manner of diffusion of hydrogen through the group.

FILM CONTOURS SHOWN BY SHADOW.

When the shadows of these film complexes were thrown on a transparent screen every detail of their structure was clearly shown. For lecture purposes an arc lamp was used to produce these shadow-

graphs, but in the laboratory a beam of parallel rays throwing the shadows on a sheet of tissue paper fixed on the side of the cubical glass chamber (containing the film-cluster), opposite to the source of light, gave means of making accurate measurements both of lines and inclinations of planes, as well as careful tracings for further study. Fig. 16 shows the shadow picture given by the quadruple column shown in Figs. 14 and 15.

WIRE MODELS OF BUBBLE CLUSTERS AND PLATEAU FRAMES.

The wire frames already mentioned can be used to build up the corresponding clusters. When they are dipped in soap solution linked films are formed on every plane outlined by the wires, because these are in the same stable relation that exists in the associated bubble group. It is then possible to insert bubble segments into the spaces between the planes and thus build up the actual cluster on a wire frame.

These form an interesting comparison with the well-known Plateau film groups, which were formed on wire frames made in the shape of geometrical solids—cube, tetrahedron, triangular prisms, etc. When such frames were dipped in soap solution linked film planes were obtained in beautiful regular formation, though not necessarily lying in the planes of the solid figure represented in skeleton by the wire, because these planes are not the stable planes of liquid films in contact. The film figures finally obtained were enclosed within the space of the skeleton figure. Thus the films initially obtained on the six faces of a skeleton cube are pulled inwards until they meet at an angle of 120° instead of the original right-angle. As a result a small vertical or horizontal square is formed at the centre with a pair of equally inclined truncated triangles radiating from each of its edges to the parallel edges of the cube; this gives eight equal truncated triangles linked by the central square. If a small bubble is included, this is drawn into a cuboid at the centre with the remaining planes as before. So with a tetrahedron, six planes are seen to be drawn inward one from each edge, to the four lines joining the apices to the centroid. This point is therefore common to the six planes which thus divide the space inside the tetrahedron into four equal and similar parts, like the conventional model of the four affinities of a carbon atom. A double tetrahedron has this appearance repeated at each end. Using an octahedron frame, we obtain six kite-shaped figures, in three perpendicular pairs, linking the three pairs of opposite vertices, and having their obtuse ends fitting alternately at the centre, while the acute ends stretch out to the apices. These six kites are connected to the twelve edges of the frame by twelve triangular planes, making eighteen films altogether.

A hexagonal prism is an interesting case illustrating the impossibility of getting more than three films to meet at one point. A wire prism of indifferent dimensions—say, with its hexagonal edge of the same order of length as its height—will give six triangular vertical films directed from each vertical edge towards the centre, where their apices are linked by a horizontal hexagon (Fig. 26). There are in addition six pairs of truncated triangular films linking top and bottom opposite hexagonal prism edges to the parallel central film hexagon, Fig. 26 (a, b, c). If the prism height is increased and

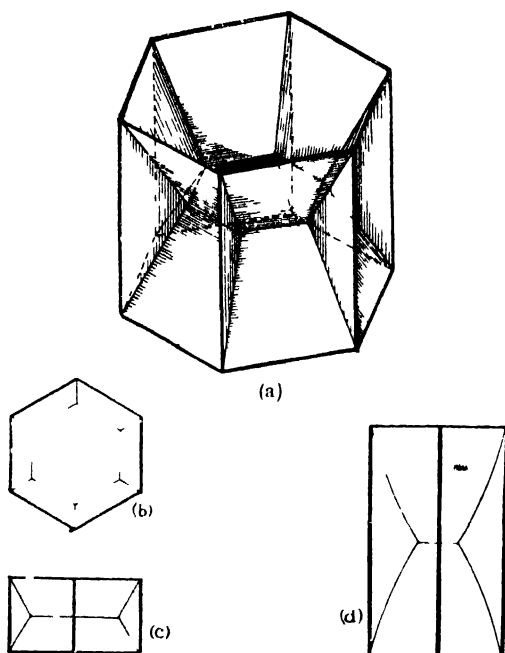


FIG. 26

this configuration preserved, then the central hexagon will decrease in dimensions and should vanish when the height of the prism is three times its hexagonal side, all the eighteen films then meeting at the centre. What happens during the process is shown in Fig. 26 (d): the central hexagon is preserved, the vertical planes are no longer triangles but have sides concave towards the apex, while the twelve remaining surfaces springing from the top and bottom edges are curved and look like a sort of hexagonal hour-glass—seen in profile (d). The condition governing all these arrangements is the equal inclinations of the tangent planes at the lines of intersection.

One interesting variation of this study was made by employing a frame composed of two thin platinum wire squares, linked by cellulose fibres vertically between the corners to form a cube, and supported by a pyramidal frame formed by four equal fibres from the upper cube corners joined together at the supporting apex. A similar pyramidal frame inverted was also formed below, the four fibres in this case being attached to a small lead weight. The resulting formation when the framework was dipped in soap solution is represented geometrically in the following three views, two elevations (*a*) and (*b*) and a plan (*c*) (Fig. 27).

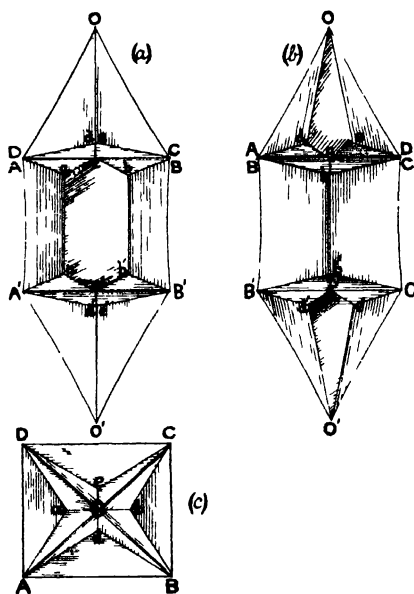


FIG. 27

This is really a combination of the cube and the octahedron patterns (already described) obtained by equally dividing the octahedron horizontally, and adding the separated portions to the top and bottom of the cube. The central square plane of the simple cube is thereby pulled out to an irregular hexagon $acbb'c'a'$ by the kite-shaped planes $Odc e$, $O'd'c'e'$, of the divided octahedron, with a consequent rearrangement of all the films at equal inclinations.

The truncated triangular films joining the vertical edges of the cube to the central (hexagon) plane then become very short. In Fig. 27 (*a*) they are shown by AaA' and BbB' , while in Fig. 27 (*b*) the other two are shown by CcC' , and by DdD' behind. All four are shown in profile in Fig. 27 (*c*) by the lines Aa , Da , Bb and Cc . The kite-shaped planes from the apices O and O' of the divided octahedron are Fig. 27 (*b*) Ode and $O'd'e'$, which in Fig. 27 (*a*) are only seen in profile—i.e. perpendicular to the central irregular hexagon $acbb'c'a'$.

The edges of the two pyramids (half-octahedrons) being OA , OB , OC , OD , $O'A'$, $O'B'$, $O'C'$, $O'D'$, then the triangular films drawn in from four upper edges are in Fig. 27 (*a*) and (*b*) OAd , OBd , Oce and ODE behind Oce . Similarly for the four lower edges. These triangular films also seen foreshortened in Fig. 27 (*c*) are indicated by the same letters.

From the upper horizontal edges of the cube there also spring four triangular films in two pairs, matched on opposite sides; those from the side edges AD , BC , Fig. 27 (*c*), go down to the central hexagon at a and b , Fig. 27 (*a*), while those from the front and back edges AB , DC , join up to the kite-shaped plane at d and e , Fig. 27 (*b*). The four films are thus shown in Fig. 27 (*c*) by ADa , BCb , and ABd , DCE . The same is repeated from the four lower edges of the cube, $A'B'$, $B'C'$, etc. There then remain two pairs of quadrilateral films linking the kites and the hexagon to the triangular films from the edges. These last are represented by $Adca$, $Bdcb$, in Fig. 27 (*a*), and $Cecb$ in Fig. 27 (*c*); the other would be $Decd$ behind $Cecb$. The same is repeated on the lower edges.

The whole complex thus numbers 31 films: 12 from the cube edges, 8 from the pyramid edges, and 8 quadrilateral films, together with the kite-shaped pair and the irregular hexagon forming the backbone of the figure.

EXTENSIBILITY OF COLUMNS.

When groups of bubbles are first formed the films of which they are constituted are rather thick, because as a rule the segments are not expanded to any great size. Owing, however, to the free drainage down the intersecting channels, the excess liquid rapidly accumulates in the lower segments, and the weight thus localised distorts or breaks the group.

Some measures were therefore made of the elongations produced by added weights in various forms. In a single column it can be seen that the upper segments are longer than those lower down; with additional loading the extension increases until parting takes place. This is illustrated in Fig. 28 (which is drawn to scale). A column of 13 bubbles is shown at (*a*) when freshly blown with air containing 7 per cent. of hydrogen. After the hydrogen had diffused

out for five minutes, the loss of buoyancy produced the sag shown in the second drawing (a), taken when rupture was imminent between the first and second segments; the measurements could not, therefore, be completed. The ratio of length to breadth of the longest segment (on the point of instability) is 1.17 to 1. Comparative measures are also shown in the two drawings (b) of the considerable contraction that takes place in an air-blown column between its early condition when uniformly coloured, with all superfluous liquid

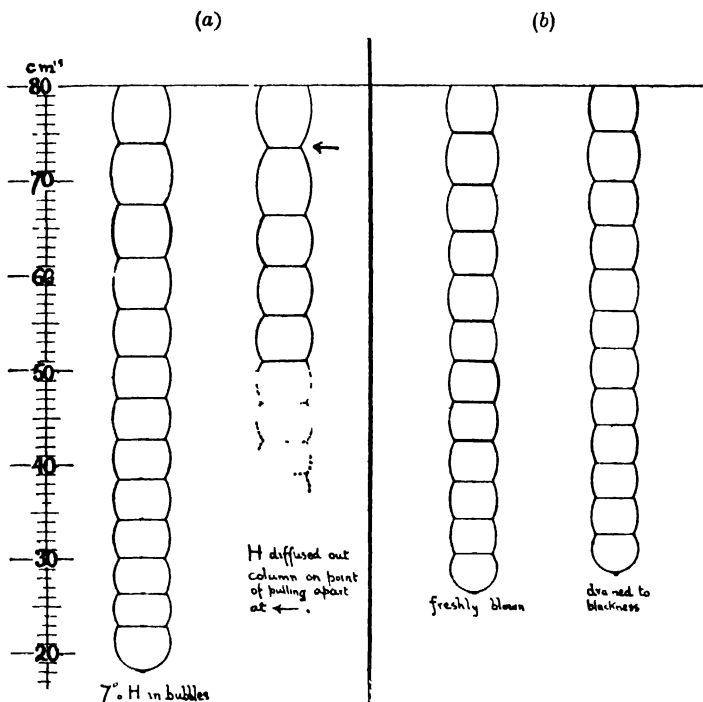


FIG. 28

removed, and its final condition of complete blackness, and therefore minimum mass. The successive heights of the segments in a column half an hour after blowing (uniformly coloured, no excess liquid) were, counting from the top, 5.1 to 5.2 cm. for the first four; then in succession, 5.0, 4.8, 4.3, 4.2, 4.0, 3.8, 3.2—at which point contact was made with a larger segment on a fixed support.

The long glass cylinder in Fig. 6 was chiefly used for these measurements. The sliding support rod was adapted for manipu-

lating a separate light glass ring, on which small weighed pieces of steel wire could be hung. A graduated pull could be exerted by a small solenoid below. Tiny horizontal magnets were attached to the columns, and by their tendency to set in the meridian were able to retard irregular oscillations. For this purpose they were fixed to light cotton rings by being soaked in nitro-cotton solution and dried.

A column of six segments each of 150 c.c. was elongated by one-third of its length with a weight of 0.136 gram; the original length, free of superfluous liquid, being 31.0 cm., and the maximum elongation, 11 cm.; the smallest additional weight then broke the column. The same weight, hung on a column of five bubbles 23 cm. long, caused an elongation of 8.3 cm., or 35 per cent. On the removal of a drop of liquid weighing six centigrams a contraction of 2.3 cm. followed.

A column of three segments gave the following result: with a weight of .075 gm. its initial length was 14.7 cm., and the elongation produced was 1.35 cm.

The following values were obtained from the gradual increase of load when a loss of buoyancy occurred by diffusion of hydrogen from a column of eight equal segments of 150 c.c. blown with 7 per cent. hydrogen. The initial length of 35 cm. was increased to 39.5 cm. when a weight of 7.5 centigrams was hung on. When the hydrogen had diffused out the total length became 40.3 cm., or an extension of 0.8 cm. from an additional weight of 8.4 milligrams. These results are recorded in the following table (I.).

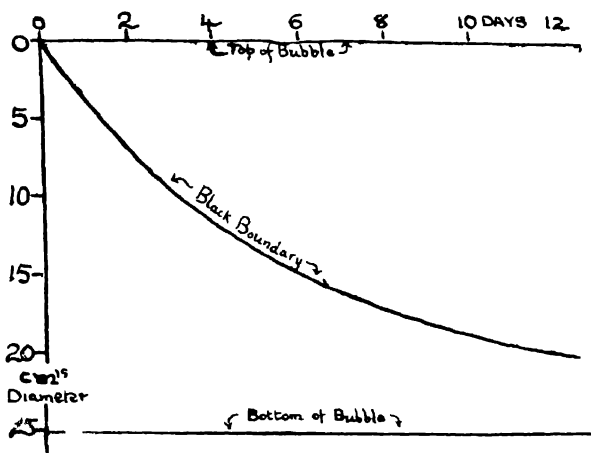
TABLE I.

<i>n</i>	<i>l</i>	<i>w</i>	<i>e</i>	<i>wl</i>	<i>x</i>	<i>wl/x</i>	<i>E</i>
	cm.	gm.	cm				
6	31	.136	11	4.22	.355	11.9	.383
5	23	.136	8.3	3.13	.361	8.7	.377
"	23	.136 .006	8.3-2.3	2.99	.261	11.5	.498
3	14.7	.075	1.35	1.10	.092	12.0	.817
8	35	.075	4.5	2.63	.129	20.4	.583
"	35	.0834	5.3	2.92	.152	19.3	.552

Where *n* is the number of segments in the column; *l* is its length in cms.; *w* is the attached weight in gms.; *e* is the elongation in cms; *x* is the elongation per unit length of column; and *E* is the corresponding value of Young's modulus.

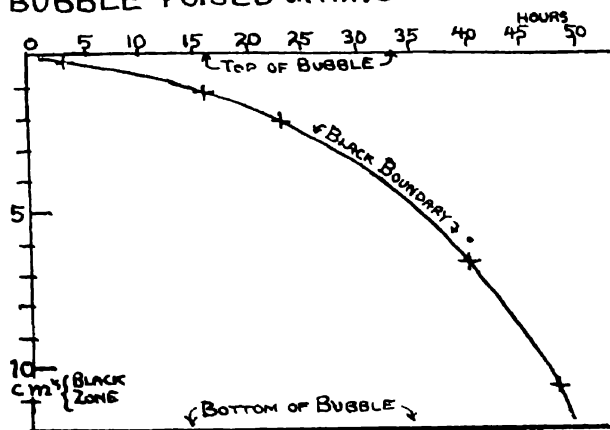
It will be noticed, on comparing the fourth set of these observations with the first set, that (roughly) halving the weight and length reduced the elongation per unit length to one-fourth, as might be expected. For, $x = \frac{e}{l}$ and $W = E \frac{e}{l}$, hence for the first case

BLACK DEVELOPMENT IN A HANGING BUBBLE



(a)

BLACK DEVELOPMENT IN BUBBLE POISED ON RING



(b)

FIG 29.

$Wl = Ee$; for the second case, $W'l' = E'e'$, or $Wl = 4 E'e'$.
 $\therefore 4 E'e' = Ee$. Now in the Table I. $E' = \cdot 817$, $E = \cdot 383$, or approximately $E' = 2 E$, hence the last equation becomes $8 e' = e$, or in terms of x , $8 x' \frac{1}{2} l = x l$, whence $4 x' = x$.

GAS TRANSFERENCE THROUGH FILM COMPLEXES.

Columns and clusters of bubbles generally reach the "black" stage with great rapidity by the action of the channels (Gibbs rings) of liquid where the segments join together. The black development of an ordinary hanging bubble is different from that of a similar bubble resting on a ring, because in the latter case the action of the Gibbs ring is to assist gravity in withdrawing liquid from the film and thus to accelerate the thinning process, while in the former case the action of the Gibbs ring is against gravity, and thus retards the withdrawal of liquid from the film. The two curves in Fig. 29 show this difference very clearly: the black boundary on the poised bubble descending at an ever-increasing rate, as it approaches the Gibbs canal present on the support ring; while in the hanging bubble the rate of fall continually decreases. (This is more noticeable when liquid is allowed to accumulate below while the thin black area extends downwards. In the absence of suitable drainage, the coloured zone then becomes continually thicker.) When however a bubble was provided with two Gibbs rings, one above and one below, the rate of fall of the black boundary was almost linear for the greater part of the time.

This was arranged by attaching a small bubble under a large one, supported as usual from a nozzle above. The small bubble was kept steady by a smaller glass ring underneath. The nozzle was 8.3 cm. in diameter, and the size of the small attached bubble was adjusted so that the diameter of the Gibbs ring of contact between the two bubbles was about the same. The greater bubble was 40 cm. high between the equal Gibbs rings top and bottom, viz. where contact was made with the nozzle above, and the small bubble film below. The graph of "black fall" plotted with time was very nearly straight for $2\frac{1}{2}$ days, by which time the black area had extended over three-fourths of the surface. After this it spread more slowly, and took another day and half to reach the lowest point. The form was therefore intermediate between curves (a) and (b) of Fig. 29.

Now, in the more complex clusters there are many channels all connected at various inclinations, therefore not only is any excess liquid quickly discharged, but the films themselves are quickly drained to the "black" state.

This is the most favourable condition for the study of gas transference, as the film is then at its minimum thickness. The resulting contraction has been measured in the case of straight columns and other complexes by photographs taken periodically. These afford

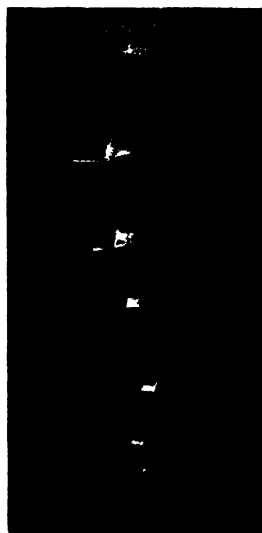
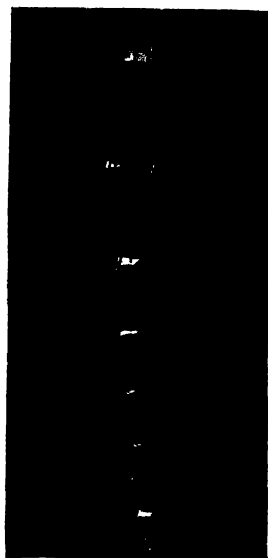


FIG. 30

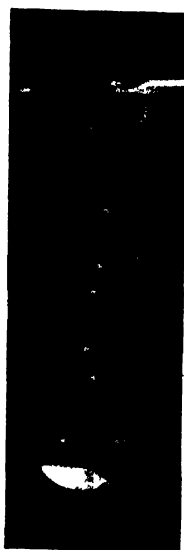


FIG. 31.

direct evidence of greater rate of transference in the smaller bubbles; for when records are taken of a column of unequal segments it is easily seen that the initial inequalities are accentuated as time goes on. Figs. 30 and 31 are reproductions from photographs of two small columns at intervals of nine and seven days respectively; the volumes of the segments varied from 30 to 100 cm.

Large black volumes were more difficult to deal with on account of irregular oscillations; their relatively small mass when black was insufficient to stabilise them against any local convection. For example, in the 200 litre globe already described a column was blown consisting of six segments, the upper five of which had each a capacity of $1\frac{1}{2}$ litres, while that of the lowest was 3 litres. In one day it became wholly black with the exception of a thick coloured area that extended up over 30 per cent. of the lowest bubble, the weight of which was sufficient to keep the whole hanging vertically, although some of the junction planes were slightly inclined. By the sixth day the colour had diminished to a zone 5 cm. wide. This reduced load could not keep the column straight, and some of the oscillations that occurred displaced the drop on the lowest bubble as much as 15 cm. from the vertical, while a vertical contraction of 15 mm. had accrued, followed in the next two days by a further contraction of $6\frac{1}{2}$ mm. The coloured zone was now a disc of 2 cm. diameter, and the column had become so curved that an unusually large oscillation caused the lowest bubble to touch the globe, with the result that only the two uppermost segments remained, the junction plane between them being inclined at 30° to the horizontal.

A light glass ring was therefore arranged below to keep the column stationary. It was sealed to a 3 mm. glass rod bent round in a bow, roughly to follow the contour of the globe, and then secured to a vertical glass rod that could slide air-tight in the rubber stopper at the neck. The contraction of the column due to the gas transference, however, went beyond the limits through which the glass rod could be raised. The segments therefore became thinner and more strained, until on the 89th day separation took place between the third and fourth. The glass ring thereupon relaxed a distance of 8 mm., the amount by which the glass bow had been strained by the pull of the black column.

In some cases the various segments were measured daily by a cathetometer and horizontal sliding telescope. If D is the diameter of a bubble segment at the equator, and d the diameter of the plane circular ends, while h is the height, then the volume is given by

$$V = 1.0472h (0.4 D^2 + 0.2 Dd + 0.15d^2).$$

When the segment is unstrained, $d = D - 0.268h$, so that

$$V = 1.0472h (0.75 D^2 - 0.130 Dh + 0.01h^2);$$

only D and h need therefore be measured.

These relations were found to agree very well with the dimensions of segments of known volume.

The area of the curved surface through which the gas transference takes place (there being practically no loss through the plane

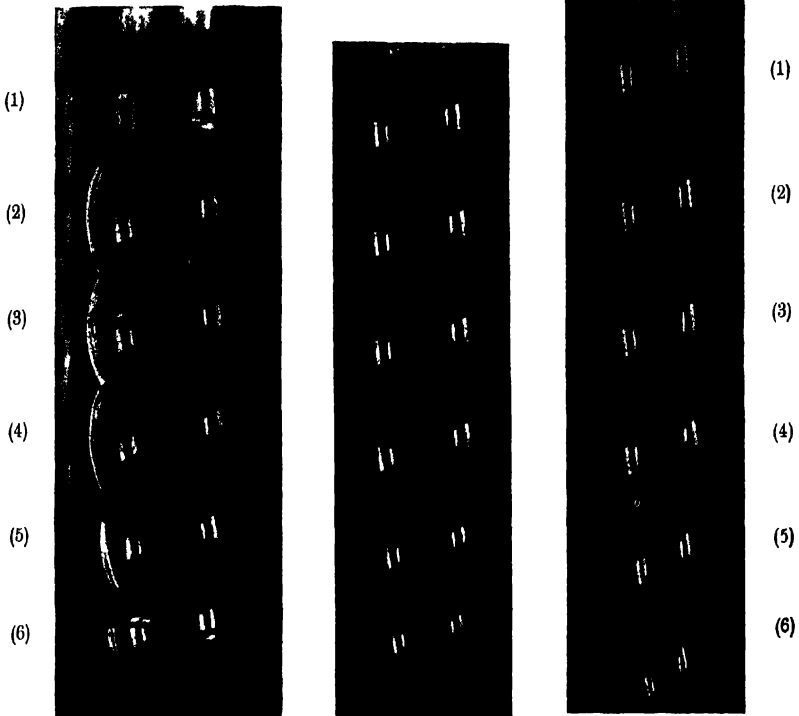


FIG. 22.

FIG. 33.

FIG. 34.

ends) is given for a bubble whose centre of curvature is not in the axis of revolution by

$$S = \frac{\pi^2}{3} l h \left(2 \frac{\pi^2}{3} - 2\pi \right) h^2 - 3.289 l h - 0.295 h^2.$$

It must be noted that an uncontracted bubble segment has been assumed. This, however, was no longer the case when it became necessary to fix the column at both ends (to a nozzle above and a glass ring below). As the contraction proceeded therefore the total length did not alter, so that h remained practically the same

throughout; but as the segments shrank *D* and *d* continually diminished. Three illustrations of this are shown in Figs. 32-34. They are taken from a column of six bubbles in the 200 litre globe already described. The four top bubbles were of equal volume, while the two lowest were half the volume of the others. The third segment being between two similar ones remained symmetrical to the end, and thus gave more reliable results. The contraction finally resulted in the column pulling apart between the fifth and sixth bubbles on the 64th day. The upper five were thus left free, but the oscillations were so persistent that only a blurred photograph was possible; this was, however, sufficient to give some measures of the free segments for comparison with those obtained when strained. Fig. 32 was taken at the start, Fig. 33 on the 16th day, and Fig. 34 on the 64th day before partition took place.

The volumes and surfaces for the third segment selected for calculation were as follows (Table II.) :—

Black Six-Bubble Chain.

TABLE II.

DIMENSIONS OF SEGMENT (3).

Time	1 (Fig. 32)	16 (Fig. 33)	64 (Fig. 34)	Days
Volume	1133	1029	543	c.c.'s
Curved Surface	360	350.5	258	(cm.) ²

TABLE III

AIR TRANSFER THROUGH SEGMENT (3).

Volume	1000	750	650	600	c.c.'s
Curved Surface	346	305	288	279	(cm.) ²
Rate of Transfer	{	c.c.'s per day	7.6	11.3	14	16	through whole surface	
			0.022	0.037	0.049	0.059	per (cm.) ²	
Volume Contraction	0.76	1.51	2.15	2.67	per cent. per day

When the values were plotted with time, contraction curves were obtained for both volume and surface. By taking tangents to the volume and time curve at successive intervals of time, the corresponding rates of gas transference $\frac{dV}{S}$ were deduced.



FIG. 35.



FIG. 36

The third segment thus gave the values shown in Table III. for air transference through the black film composed of $3\frac{1}{2}$ per cent ammonium oleate and 33 per cent glycerin.

Three sets of these columns in the 200 litre globe were tried. The first was the largest in volume, and took 101 days to pull apart. Figs. 35 and 36 show the appearances at start and finish, the total

length meantime had been reduced from 53.3 to 50.9 cm.; after this the free bubbles remained on the nozzle a further 53 days. They were then replaced by the second set already described, which took 64 days before it divided. The third set which followed was more uniform, consisting of one segment, top and bottom, each of whose volumes was half a litre, while the four in the middle contained one litre each. This set parted in 40 days.

Very good black columns were also obtained in the long glass cylinder (Fig. 6). With this it was possible to prevent undue straining of the segments by carefully raising the support ring when necessary. The cylinder was long enough to get in ten segments, each of over 250 c.c. A thin thread of stranded cellulose (artificial silk) was sometimes fixed both at the nozzle and support ring to lie along the outer contour of the column from top to bottom. This not only stabilised the column while being blown, but accelerated the drainage and black development, because any excess liquid in the Gibbs ring channels of the junction planes was quickly drawn into the capillary canals of the silk. The result was that the black stage was complete in one day, and there was entire absence of any deformation from superfluous liquid remaining in the junction rings. One set took 47 days before the shrinkage caused the segments to part, the support ring not having been raised. The ratio of length to breadth of the equal segments two days before this occurred was 1.5:1, as compared to 1.17:1 in a similar coloured column of like dimensions, but without any cellulose thread, and dragged apart by loading (see Fig. 28).

The segment volumes of another set diminished during the first fortnight from about 270 c.c. to 225 c.c., and the curved surfaces from 145 to 120 square centimetres. The calculated rates of air transference obtained from the contraction curves, are given in Table IV.; the solution used contained 5 per cent ammonium oleate and 50 per cent glycerin.

TABLE IV.

Volume	265	250	235	c c.'s
Curved Surface	143	139.5	196	(cm.) ²
Rate of Transfer	} o.c.'s per day		1.83	3.62	5.24	through whole surface	
			0.013	0.026	0.039	per (cm.) ²	
Volume Contraction	0.69	1.45	2.23	per cent per day	

Much higher values were given by a black column of five equal segments, initially 161 c.c., very completely drained by two cellulose strands on opposite sides of the bubble contours. No glass ring support was employed, so that the column contracted freely without the segments being strained out of their normal curvature. In four days the volume diminished 30 per cent. The mean rate of air transference being nearly 11 c.c. per day when each segment had a volume of approximately 125 c.c. The corresponding value of the curved surface was about 80 (cm.)^2 , so that the loss through unit area was 0.14 c.c. per day. The solution used for this contained 1 per cent ammonium oleate to 10 per cent. of glycerin.

GAS DIFFUSION THROUGH BLACK FILMS.

The rate at which gases diffuse through liquid films was found to be very much greater than the slow escape caused by the small excess-pressure by which bubbles are distended. The latter only becomes appreciable some days after the black stage is reached; but if a thick coloured air bubble has a small percentage of hydrogen blown into it, a contraction takes place in a few minutes; or, conversely, an expansion is quickly produced by circulating some hydrogen in the closed vessel in which the bubble is hanging. In the same way when a plane film was formed across a cylindrical vessel containing only air and some soap solution, and hydrogen was then circulated in the space between the film and the neck, a steady movement of the film towards the neck at once began; the hydrogen passed through to the enclosed space beyond the film more quickly than the contained air diffused out. The reverse process was easily carried out by first filling the bottle with pure hydrogen, and expanding the film as before. A current of clean air was then circulated on the same side of the film as before; the resulting movement of the film was now away from the neck, because the volume enclosed beyond the film lost hydrogen more quickly than air could diffuse in. When oxygen was used instead of air the motion was more rapid.

When these experiments were made after the black stage was reached, the diffusion was sufficiently rapid to cause a large distortion of the plane film, due to partial adhesion round the periphery of the film, although the glass walls had previously been well moistened. For the laboratory measures of the relative diffusion rates of various gases, an 8 litre bottle, 19 cm. in diameter, was calibrated, and the movements of the film (which would thus have an area of some 300 cm.^2) were noted for successive small time intervals. The stopper was fitted with inlet and outlet tubes, of which the former was long enough to reach the bottom, and could also slide easily in an airtight fitting. The film was thereby started by pushing the inlet tube down

into a small quantity of soap solution in the bottle, and then withdrawing it gradually as the gas current expanded it to the desired position. The tube was then pulled just through the film, the current nearly shut off, and the whole left to settle until the black zone had developed sufficiently in the film. The gas to be circulated was then connected and turned on, and the movements of the film noted. The end of the outlet tube was kept within a cm. of the film surface to maintain a thorough circulation.

With hydrogen in the vessel, and when the film was half black and half silvery (next in thickness to black), and air was circulating at 130 c.c. per minute, the volume enclosed by the film decreased at a fairly uniform rate of 1 litre in 20 minutes. After this the movement became slower as the percentage of hydrogen diminished in the space beyond the film. Finally, 5.70 litres of hydrogen originally present were found to be replaced by 1.40 litre of air. In another experiment, with the film almost completely black, 6.23 litres of hydrogen diffused out and were replaced by 1.35 litre of air.

The maximum rate of diffusion could not be realised in this wide vessel because of the film distortion that was produced when the rate of circulation was increased. To overcome this a vessel only 8.5 cm. in diameter was used (Fig. 37), in which the ordinary stopcock was replaced by a two-way cock A, while an inlet and outlet fitting was fixed in the rubber stopper. The outlet tube as before could slide easily in its airtight neck. The vessel was filled with hydrogen coming in through A and leaving at B. The film was obtained (after first moistening the walls of the vessel) by tilting a drop of the soap solution into the neck at A. The gas entering there

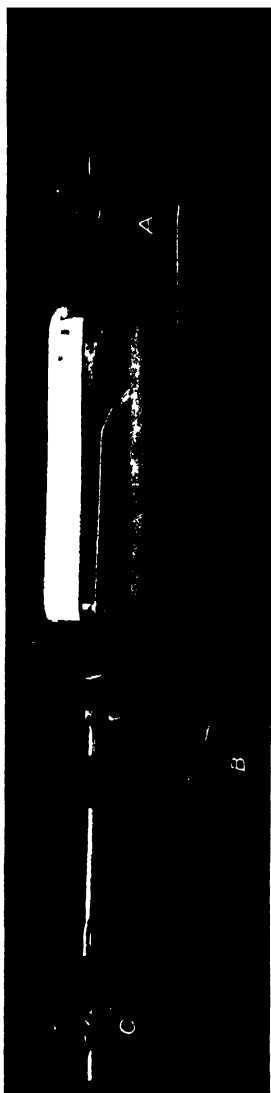


Fig. 37.

at once formed a film and pushed it along to the desired position. A was then closed and the film left to become black. Meanwhile a small current of hydrogen was continued through B and C to prevent any subsequent disturbance of the film, such as by an alteration of temperature.

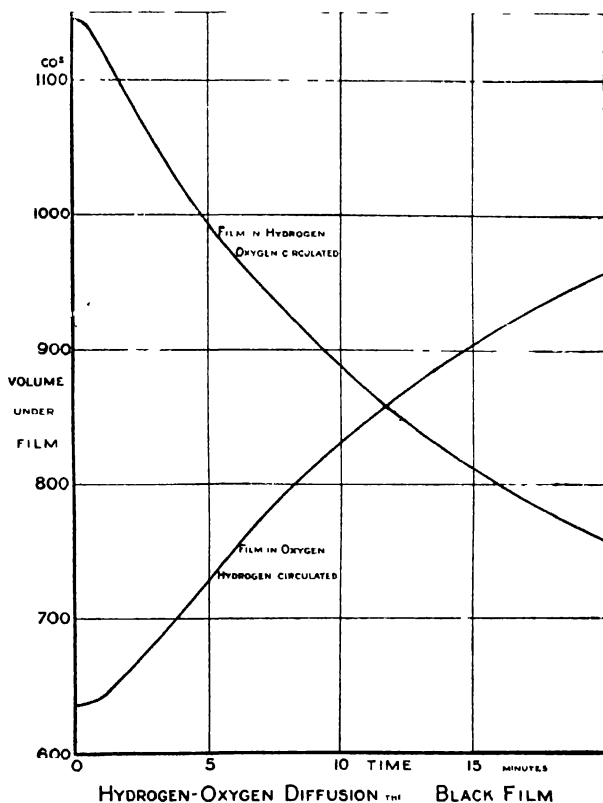


FIG. 38.

Before starting the air or oxygen current through B and C the film was lubricated by a slow complete revolution of the vessel, whereby the small amount of liquid inside flowed all round the walls. This caused some diminution of the black area, which was measured and allowed for. During the subsequent diffusion the

sliding tube was adjusted so that its open end was kept within a centimetre of the moving film. Small measured samples of the mixed gases behind the films were withdrawn at intervals for analysis through the two-way cock A.

The maximum rate of diffusion of hydrogen above that of air was found to be 42 c.c. per hour per cm^2 . When oxygen was used instead of air the value obtained was 50 c.c. of hydrogen per hour per cm^2 greater than the oxygen going the other way; and 1145 c.c. of hydrogen passed out, while 632 c.c. of oxygen went in. When the reverse process was tried 1173 c.c. of hydrogen went in through the black film, while 635 c.c. of oxygen diffused out. The two operations involved the passage of the film 7 cm. along the cylinder in the first case, and the same back again for the reversal. Fig 38 gives the graphs of the movement of the film, and shows the variation of the enclosed volume, with the time. The rate of relative diffusion at any time is given by the slope of the tangent to volume-time curves. This was found to decrease as the proportion of oxygen under the film increased.

The contraction of bubbles in air when blown up with from 10 per cent. to 30 per cent. of hydrogen was measured in order to deduce the diffusion rates through coloured films. A much lower value was obtained; thus a bubble coloured steely blue to pale amber and containing 16 per cent. of hydrogen showed a rate of contraction of approximately $\frac{2}{3}$ c.c. per hour per cm^2 . Measures were also made with half bubbles blown on the roof of a glass chamber in which a proportion of hydrogen was circulated; and also by comparing the contractions of similar bubbles when hanging from a nozzle and resting on a ring. This last was done to correct for the distortion of figure produced by the buoyancy of the contained hydrogen.

HYDROGEN BUBBLES BLOWN UNDER SEVERAL ATMOSPHERES.

Bubbles that have thinned to blackness contract at an ever-increasing rate by the continual transference of the enclosed gas through the envelope. It was mentioned in last year's Discourse that this contraction is greatly retarded when the bubbles are formed in an enclosure in which the pressure has been raised, the excess-pressure distending the bubble becoming then of relatively smaller proportion to the total pressure. Further experiments have shown that a black bubble in hydrogen under 6.3 atmospheres pressure took 100 days for its diameter to contract from 7.7 to 4.0 cm, whereas only 7 to 10 days is needed for the same contraction to take place in a similar bubble at atmospheric pressure. When air was used instead of hydrogen the difference was equally marked; thus

an 8 cm. bubble in a vessel charged to 7 atmospheres took 4 months to diminish 1 cm. in diameter, the same contraction at atmospheric pressure taking only about 14 days.

Suitable vessels for these measurements are afforded by the strong glass bottles used to hold sulphurous acid. A screwed brass collar



FIG. 39.

was cemented to the neck, and to this a brass T-piece was secured by a gas-tight union. The glass nozzle for supporting the bubble was cemented into the vertical arm of the T-tube, and sealed to a thick glass bulb above bent over horizontally to hold some soap solution. The gas used was admitted by the valved horizontal arm of the T-piece, a hole being made at this level into the inner glass tube to give access through the nozzle, which had a diameter of about 1 cm. (Fig. 39). Just within its lower end a constriction was formed. The apparatus was tested and found tight under 10 atmospheres pressure.

The pressure was first adjusted to about 6 atmospheres, and a drop of soap solution was decanted into the constriction; on admitting more gas a bubble was expanded on the nozzle and the pressure thereby raised to $6\frac{1}{2}$ atmospheres. The black stage then developed very much as usual, and the gas transference was determined by periodic measurements of the contraction.

Table V. gives the rate of transference obtained in hydrogen at $6\frac{1}{2}$ atmospheres compared with the values at 1 atmosphere. The numbers given are calculated for diameters of 4, 6 and 8 cm. The second column gives the internal excess pressure P of the soap bubble (in mm. of water) measured at atmospheric pressure. The proportion F of this to the total pressure in the bubble vessel is shown in the third column (in units of 10^{-6}) both for 1 atmosphere and $6\frac{1}{2}$ atmospheres. The observed rates of gas transference R are similarly shown in the fourth column.

TABLE V.

Diameter cm.'s	P mm.'s H ₂ O	F × 10 ⁻⁶		R c.c.'s	
		(a) 1 atm.	(b) 6.5 atm.	(a) 1 atm.	(b) 6.5 atm.
4	0.330	32.16	4.80	0.22	0.0825
6	0.220	21.44	3.20	0.14	0.041
8	0.166	16.08	2.40	0.10	—

Thus it may be said that the longevity is increased in the proportion of the numbers given in the last two columns, in this case, approximately as the square roots of the relative pressures under which the bubbles were blown.

For experimental assistance I have to thank W. J. Green, B.Sc., and for reading the proofs and checking the calculations, I am indebted to J. D. H. Dickson, M.A., Senior Fellow of Peterhouse College, Cambridge.

[J. D.]

Friday, January 25, 1918.

SIR WILLIAM PHIPSON BEALE, Bart., K.C. M.P.,
Vice-President, in the Chair.

PROFESSOR JOHN S. TOWNSEND, F.R.S.

The Motions of Ions in Gases.

WHEN ions move in a gas under an electric force, and the sizes of the ions are unaffected either by changes of force or of pressure, the velocity of the ions in the direction of the force is proportional to the ratio of the force to the pressure (X/P), provided the velocity in the direction of the force is small compared with the velocity of agitation of the ions. For small values of the ratio X/P the ions move as if they were associated with masses which are large compared with the masses of the molecules of the surrounding gas, and the kinetic energy of the motion of agitation of the ions is equal to that of the molecules with which they collide.

When the pressure is reduced the mobility of the negative ions increases with the force, which shows that the mass associated with each ion diminishes as the force increases.

Experiments were described from which it was shown that at a certain point, depending on the ratio X/P , the electrons move freely through the gas, as the ratio of the charge e to the mass m of the electrified particle was found to be approximately the same as the value 5.6×10^{17} for electrons moving in a highly exhausted space.

Thus in dry air at a pressure of 18 millimetres of mercury the electrons move freely, unassociated with larger masses, when the force is 3 or 4 volts per centimetre. A similar result is obtained at higher pressures by increasing the force. When a small quantity of water vapour is present in the gas a larger force is required to attain the point at which the electrons move freely, which shows that the electrons have a greater tendency to adhere to molecules of water vapour than to molecules of oxygen or nitrogen.

In all cases the electronic state is attained with much smaller forces than those required to produce ions by collisions with molecules. The latter effect, for example, could not be easily detected in air at 18 millimetres pressure unless the force exceeded 30 volts per centimetre.

The experiments show that while the mass associated with the electron undergoes these changes the charge remains constant.

It was also found that after the transition stage from the large to the small mass, the velocity of agitation of the electrons is much larger than the velocity corresponding to that of a particle of equal mass in thermal equilibrium with the surrounding gas. The latter velocity is approximately 10^7 centimetres per second, whereas the velocity of agitation of the electrons is 1.6×10^7 centimetres per second in dry air, when $X/P = 0.2$. This velocity increases with the force and is 10^8 centimetres per second, when $X/P = 50$.

The velocity of agitation of the electrons is easily deduced from observations on the lateral diffusion of a stream of particles moving through the gas under an electric force. The spreading of the stream is independent of the pressure of the gas, and has a definite normal value depending on the force when the kinetic energy of agitation of the ions or electrons is equal to that of the surrounding molecules. When the pressure is reduced below a certain value, which is proportional to the force, the lateral diffusion becomes abnormally large, which can only be due to an increase in the velocity of agitation of the electrons.

This result* shows that the electrons tend to retain the velocity they acquire under the electric force, and the principal effect of a collision with a molecule is not to reduce the velocity of an electron, but only to alter its direction of motion. This action continues until a steady state is attained in which the motion of agitation is so large that the loss of energy by collisions is equal to the energy acquired under the electric force.

[J. S. T.]

Friday, February 1, 1918.

J. H. BALFOUR BROWNE, K.C. LL.D., Vice-President,
in the Chair.

PROFESSOR A. S. EDDINGTON, F.R.S.

Gravitation and the Principle of Relativity.

THERE were many difficulties to encounter in entering the room just now. To begin with, we had to bear the crushing load of the atmosphere, amounting to 14 lbs. on every square inch. At each step forwards, it was necessary to tread gingerly on a piece of ground moving at the rate of 20 miles a second on its way round the sun. We were poised precariously on a globe, apparently hanging by our feet, head outwards into space. And this acrobatic feat was performed in the face of a tremendous wind of ether, blowing at I do not know how many miles a second literally through us. We do not claim much credit for overcoming these difficulties—because we never noticed them. But I venture to remind you of them, because I am about to speak of some other extraordinary things that may be happening to us of which we are quite unconscious.

Not to go too far back in history, the present subject arises from a famous experiment performed in the year 1887, known as the Michelson-Morley experiment. The apparatus was elaborate, but the principle of the experiment is not very difficult. If you are in a river, which will be the quicker—to swim to a point 50 yards up stream and back again, or to a point 50 yards across stream and back again? Mathematically the answer is, perhaps, not immediately obvious, because the net effect of the current is a delay in both cases. But I think that anyone who has swum in a river will have no hesitation about the answer. The up-and-down journey takes longer. Now we *are* in a river—of ether. There is a swift current of ether flowing through this room; or, if we happen to be at rest in the ether at the present moment, six months hence the earth's orbital motion will be reversed, and then there must be a swift current. Michelson divided a beam of light into two parts; he sent one half swimming up the stream of ether for a certain distance, and then by a mirror back to the starting-point; he sent the other half an equal distance (as he thought) across the stream and back. It was a race; and with his apparatus he could test very accurately which part got back first. To his surprise, it was a dead-heat. Clearly the two paths could not really have been equal, the along-stream path must have been a little

shorter to compensate for the greater hindrance of the current. That objection was foreseen, and the apparatus, which was mounted on a stone pier floating in mercury, was rotated through a right angle, so that the arm which was formerly along the stream was now across the stream, and *vice versa*. Again, the two portions of the beam arrived at the same moment; so this time the other arm had become the shorter—simply by altering its position. In fact these supposedly rigid arms had contracted when placed in the up-and-down stream position by just the amount necessary to conceal the effect which was looked for.

That is the plain meaning of the experiment; but we might well hesitate to accept this straightforward interpretation, and try to evade it in some way, were it not for some theoretical discoveries made later. It has gradually appeared that matter is of an electrical nature, and the forces of cohesion between the particles, which give a solid its rigidity, are electrical forces. Larmor and Lorentz discovered that this property of contraction in the direction of the ether current was something actually inherent in the formulæ for electrical forces written down by Maxwell many years earlier and universally adopted; it only waited for some mathematician to recognize it. It would be going too far to say that Maxwell's equations actually prove that contraction must take place; but they are, as it were, designed to fall in line with the contraction phenomenon, and certain details left vague by Maxwell have since been found to correspond.

We are then faced with the result that a material body experiences a contraction in the direction of its motion through the ether. According both to theory and experiment the contraction is the same for all kinds of matter—a universal property. One reservation should be made; the experiment has only been tried with solids of laboratory dimensions, which are held together by *cohesion*. There is at present no experimental evidence that a body such as the earth whose form is determined by *gravitation* will suffer the same contraction; we shall however assume that the contraction takes place in this case also.

I am going to ask you to suppose that we in this room are travelling through the ether at the rate of 161,000 miles a second, vertically upwards. Let us be bolder and say that that is our velocity through the ether—because no one will be able to contradict us. No experiment yet tried can detect or disprove that motion; because all such experiments give a null result, as the Michelson-Morley experiment did. With that speed the contraction is just one-half. This pointer, which I hold horizontally, is 8 feet long. Now [turning it vertically] it is 4 feet long. But, you may say, it is taller than I am, and I must be approaching 6 feet. No, if I lay down on the floor I should be, but as I am standing now I am under 3 feet. The contraction affects me just as it did the pointer. It is no use bringing a standard yard-measure to measure me, because that also will con-

tract and represent only half a yard. "But we saw that the pointer did not change length when it turned." How did you tell that? What you perceived was an image of the pointer on the retina of your eye, and you thought the image occupied the same space of retina in both positions; but your retina has also contracted in the vertical direction without your knowing it, so that your estimates of length in that direction are double what they should be. And similarly with every test you could apply. If everything undergoes the same change, it is just as though there were no change at all.

We thus get a glimpse of what from our present point of view must be called the *real* world, strangely different from the world of appearance. In the real world, by changing position you extend yourself like a telescope; and the stoutest individual may regain slimmness of figure by an appropriate orientation. It must be something like what we see in a distorting mirror; and you can almost see a living-picture of this real world reflected in a polished door-knob.

If our speed through the ether happens not to be so great as we have supposed, the contraction is smaller; but it escapes notice in our practical life, not because it is small, but because from its very nature it is undetectable. And because this real world is undetectable we do not as a rule attempt to describe it. Not merely in everyday life, but in scientific measurements also, we describe the world of appearance. We do this by imagining natural objects to be placed, not in the absolute space, but in a quite different framework of our own contriving—a space which corresponds to appearance. In the space of appearance a rod does not seem to change length when its direction is altered; and we use that property to block out our conventional space, counting the length occupied by the standard yard-measure as always a yard however its true length may vary. It is found also that in like manner our time is a special time of our own, different from the time we should adopt if our motion through the ether were nil. This is a perfectly right procedure; it introduces no scientific inexactness, and it is more in accordance with the ordinary meaning attached to space and time; the only thing to remember is that this space and time framework is something peculiar to us, defined by our motion, and it has not the metaphysical property of absoluteness, which we have often unconsciously attributed to it.

Now let us visit for a moment the star Arcturus, which is moving relatively to us with a velocity of over 200 miles per second. Consequently its motion through the ether is different from ours, and the contraction of objects on it will be different. It follows that our conventional space would not be suitable for Arcturus, because it was specially chosen to eliminate our own contraction effects. There is a different space and a different time proper to Arcturus. We must then imagine each star carrying its own appropriate space

and time according to its motion through the ether. The space and time of one star will not fit the experience of individuals on another star.

The exact relation between the appropriate space and time of one star and the space and time of another was first brought out clearly by Minkowski; it is a very remarkable one. We recognize three dimensions of space, which we may take as up-and-down, right-and-left, backwards-and-forwards. If we go over to Ireland we still have the same space, but Ireland's up-and-down no longer corresponds to ours. The directions are inclined; and what is vertical to them is partly vertical and partly horizontal to us. Now let us add a fourth dimension, imaginary* time, at right angles to the other three. There is no room for it in the model, but we must do our best to imagine it in four dimensions. In Ireland the three space-dimensions will have rotated, as I have said; but the time will be just the same. But if we go to Arcturus, or to any body moving with a velocity different from our own, the time-dimension also has rotated. What is time to them is partly time and partly imaginary space to us. It is a change in the space-time world of four dimensions just analogous to the change in the space-world between here and Ireland. That is Minkowski's great result; space-time is the same universally, but the orientation—the resolution into space and time separately—depends on the motion of the individual experiencing it, just as the resolution of space into horizontal and vertical depends on his situation. In Minkowski's own famous words—"Henceforth Space and Time in themselves vanish to shadows, and only a kind of union of the two preserves an independent existence."

From our original point of view it seems very remarkable that in the Michelson-Morley experiment the contraction should have been of just the right amount to annul the expected effect of our motion through the ether. Many other experiments, which seemed likely to show such an effect, have been tried since then, but in all of them the same kind of compensation takes place. It looks as though all the forces of nature had entered on a conspiracy together with the one design of preventing us from measuring or even detecting our motion through the ether. It is still an open question whether one force, the force of gravitation, has joined the conspiracy. Hitherto gravitation has stood aloof from all the other interrelated phenomena in majestic isolation. We have become almost reconciled to leaving it outside every physical theory. A new model of the atom is put forward which accounts for a whole host of abstruse and recently discovered properties; but it would be considered unfair to suggest that it ought to account for the simple and universal property of gravitation. Dare we think that gravitation has so far forgotten its

* Imaginary in the mathematical sense, i.e. involving $\sqrt{-1}$.

dignity as to join this conspiracy? There is certainly not enough evidence for a jury to convict; but yet I think we shall have to intern it on suspicion. Recently Sir Oliver Lodge, believing that gravitation was innocent of the conspiracy, showed that a very famous astronomical discordance in the motion of Mercury might be an effect due to the sun's motion through the ether, and might afford a means of estimating its speed. It is difficult in a brief reference to deal quite fairly with an intricate question, but it seems now that we should rather lay stress, not on this single discordance, which can perhaps be otherwise explained, but on the exact agreement of Venus and the Earth with theory; for they also should show evidence of the sun's motion through the ether if gravitation had not joined in the conspiracy to conceal all such effects. It may be that the effects on Venus and the Earth are not found because the sun's motion through the ether happens to be very small; but on the whole it appears more likely that the effect of the motion is null, just as in the Michelson-Morley experiment, because there is a complete compensation in the law of gravitation itself.

The great advantage of Minkowski's point of view is that it gets rid of all idea of a conspiracy. You cannot have a conspiracy of concealment when there is nothing to conceal. We cut Minkowski's space-time world in a certain direction, so as to give us separately space and time as they appear to us. We have been imagining that there exists some direction which would separate it into a real and absolute space and time. But why should there be? Why should one direction in this space-time world be more fundamental than any other? We do not attempt to cut the space-world in a particular direction so as to give us the *real* horizontal and vertical. The words horizontal and vertical have no meaning except in reference to a particular spot on the earth. So for a particular observer the space-time world falls apart into its four components, up-and-down, right-and-left, backwards-and-forwards, sooner-and-later; but no observer can say that this division is the one and only real one.

Our idea of a real space more fundamental than our own was, however, not entirely metaphysical; we had materialized it by filling it with an ether supposed to be at rest in it. We now deny the existence of any unique framework of that kind. We have failed to obtain experimental knowledge of such a framework since we cannot detect our motion relative to it. Whatever may be the nature of the ether, it is devoid of those material properties which could constitute it a framework of reference in space. We can perhaps best picture the ether as a four-dimensional fluid filling uniformly Minkowski's space-time *continuum*, not as a material three-dimensional fluid occupying space and time independently.

The position we have now reached is known as the Principle of Relativity. In so far as it is a physical theory, it seems to be amply confirmed by numerous experiments (except in regard to gravitation).

In so far as it is a philosophical theory, it is no more than a legitimate and useful point of view. I now pass on to a Generalized Principle of Relativity, in which we must be content at first to be guided by a natural generalization of these results, hoping later to be able to check our tentative conclusions by experiment.

If we analyze any scientific observation, distinguishing between what we perceive and what we merely infer, it always resolves itself into a *coincidence* in space and time. A physicist states that he has observed that the current through his coil is 5 milliamperes; but what he actually saw was that the image of a wire thrown by his galvanometer *coincided* with a certain division on a scale. He measures the temperature of a liquid, but the observation is the *coincidence* of the top of the mercury with a division on the thermometer. If then we had to sum up the whole of our experimental knowledge, we should have to describe it as consisting of a large number of coincidences.

A complete history of the progress of a particle consists of a knowledge of its path and the time at which it occupied each point of the path. The time may be regarded as an extra co-ordinate corresponding to a fourth dimension, and so the whole history may be summed up by a line in four dimensions representing the particle's progress through space and time. We call this four-dimensional line the *world-line* of the particle. Imagine that we have drawn the world-lines of all the particles, light-waves, etc., in the universe; we shall then have a complete history of the universe. It will be rather a dull history-book; the Venus of Milo will be represented by an elaborate schedule of measurements, and Monna Lisa by a mathematical specification of the distribution of paint; still they are there, if only we can recognize them. I have here a history of the universe—or part of it. Unfortunately I was not able to draw it in four dimensions, and even three dimensions presented difficulties, so I have drawn the world-lines in two dimensions on the surface of a football bladder.

A great deal is shown here which properly speaking is not history at all, because it is necessarily outside experience. As we have seen, it is only coincidences—the intersections of the world-lines—that constitute observational knowledge; and, moreover, it is not the place of intersection but the fact of intersection that we observe. I am afraid the two-dimensional model does not give a proper idea of this, because in two dimensions any two lines are almost bound to meet sooner or later; but in three dimensions, and still more in four dimensions, two lines can and usually do miss one another altogether, and the observation that they do meet is a genuine addition to knowledge.

When I squeeze the bladder the world-lines are bent about in different ways. But I have not altered the history of the universe, because no intersection is created or destroyed, and so no observable event is altered. The deformed bladder is just as true a history of

nature as the undeformed bladder. The bladder represents Minkowski's space-time world, in which the world-lines were drawn; so we can squeeze Minkowski's world in any way without altering the course of events. We do not usually use the vulgar word squeeze; we call it a *mathematical transformation*, but it means the same thing.

The laws of nature in their most general form must describe correctly the behaviour of the world-lines in either the undistorted or the distorted model, because it is indifferent which we take as the true representation of the course of nature. That is a very important principle; but, being almost a truism, it does not in itself help us to determine the laws of nature without making some additional hypothesis. There is one law—the law of gravitation—which especially attracts our attention at this point, and we shall look into it more closely.

We know that one particle attracts another particle, and so influences the history of its motion. This evidently means that one world-line will deflect any other world-line in its neighbourhood. Apart from this influence, the world-line runs straight, bending neither to the right nor to the left, provided the bladder is in its undistorted state, i.e. provided we use Minkowski's original space-time. That is not so much a matter of observation as of definition. It defines what we are to regard as the undistorted state, though it is by observation that we learn that it is possible to find a space-time in which the world-lines run straight when undisturbed by gravitational or other forces. I must own that there is a certain logical difficulty in saying that a world-line runs straight when there are no others near it; because in that case there could be no intersections, and we could learn nothing about its course by observation. However, that is not a serious difficulty, though you may be reminded of the sage remark, "If there were no matter in the universe, the law of gravitation would fall to the ground."

We have to admit, then, that a world-line can be bent by the proximity of other world-lines. It can also be bent, as you see, by the proximity of my thumb. The suggestion arises, may not the two modes of bending be essentially the same? The bending by my thumb (a mathematical transformation of space and time) is in a sense spurious; the world-line is pursuing a course which is straight relative to the *original* material. Or we may perhaps best put it this way—the world-line still continues to take the shortest path between two points, only it reckons distance according to the length that would be occupied in the unstretched state of the bladder. It is suggested that the deflection of a world-line by gravitation is of the same nature; from each world-line a state of distortion radiates, as if from a badly puckered seam, and any other world-line takes the shortest course through this distorted region, which would immediately become straight if the strain could be undone. The

same rule - of shortest distance as measured in the undistorted state -- is to hold in all cases. This is a mode of reasoning which has often been fruitful in scientific generalizations. A magnetic needle turns towards the end of a bar-magnet; it also turns towards a spot near the pole of the earth; hence the suggestion that the earth is a magnet. We assume the essential identity of the two modes of deflecting the needle. It is a daring step to apply the analogy, and assume the essential identity of the two ways of deflecting world-lines; but at any rate we shall make this assumption and see what comes of it.

You will see that according to this view the earth moves in a curved orbit, not because the sun exerts any direct pull, but because the earth is trying to find the shortest way through a space and time which have been tangled up by an influence radiating from the sun. We can continue to describe this indirect influence of the sun on the earth's motion as a "force"; but, assuming that it makes itself felt as a modification or strain of space and time, we are able to bring the discussion of the laws of this force into line with the discussion of the laws of space and time, i.e. the laws of geometry. Needless to say we could not determine a physical law like the law of gravitation by geometrical reasoning without making some assumption.

I am afraid that to talk of a force as being a distortion of space and time must at first appear to you hopeless jargon. But it must be remembered first that we are not concerned with any metaphysical space and time. We mean by space and time simply a scaffolding that we construct as the result of our measures; and if anything queer happens to our measuring apparatus, the scaffolding may easily go crooked. Taking our everyday conception of space, we should say that this room is at rest; we have been told that it is being carried round the earth once a day, but in practical life we never pay any attention to that. The space that we naturally use is thus different from, and it is not difficult to show that it is distorted as compared with, the more fundamental astronomical space in which this room is travelling at a great velocity. So our scaffolding is crooked. But, it may be asked, in what way can this distortion of our space-scaffolding be regarded as a force? The answer is quite simple. We perceive it as a force, and that is the only way in which we do perceive it. We do not perceive that this room is being carried round by the earth's rotation, but we perceive a certain force -- the earth's centripetal force. It is rather difficult to demonstrate this force, because gravitation predominates overwhelmingly; but if gravity were annihilated we should have to be tied down to the floor to prevent our flying up to the ceiling, and we should certainly feel ourselves pulled by a very vigorous centrifugal force. That is our only perception of the crookedness of our scaffolding.

We often call the centrifugal force an "unreal" force, meaning that it arises simply from a transformation of the framework of reference. Can we feel confident that gravitation is in any sense

more "real"? In effect they are so much alike that even in scientific work we speak of them in one breath. What is called the value of gravity in London, 981.17 cm./sec^2 , is really made up partly of the true attraction of the earth and partly of the centrifugal force. It is not considered worth while to make any distinction. Surely, then, it is not a great stretch of the imagination to regard gravitation as of the same nature as centrifugal force, being merely our perception of the crookedness of the scaffolding that we have chosen.

If gravity and centrifugal force are manifestations of the same underlying condition it must be possible to reduce them to the same laws; but we must express the laws in a manner which will render them comparable. There is a convenient form of Newton's law, which was given by Laplace and is well known to mathematicians, which describes how the intensity at any point is related to the intensity at surrounding points—or, according to our interpretation, how the distortion of space at any point fits on to the distortion at surrounding points. It is evidently an attempt to express the general laws of the strains in space and time which occur in nature. If we are correct in our assumption that gravitation involves *nothing more* than strain of space-time, so that its law expresses merely the relation between adjacent strains which holds by some natural necessity, clearly the strains which give the centrifugal force must obey the same general law. Here a very interesting point arises. We cannot reconcile the Newtonian law of gravitation with this condition. Newton's law and the law of centrifugal force are contradictory.

To put the matter another way, if we determine the strains by Newton's law, we get results closely agreeing with observation, provided Minkowski's space-time is used; but if we avail ourselves of our right to use a transformed space-time, the results no longer agree with observation. That means that Newton's law involves something which is not fully represented by strains, and so does not agree with our assumption. We must either abandon our assumption, or abandon the famous law which has been accepted for over 200 years, and find a new law of gravitation which will fall in with our requirements.

This amended law has been found by Einstein. It appears to be the only possible law that meets our requirements, and in the limited applications which come under practical observation is sufficiently close to the old law that has served so well. In practical applications the two laws are indistinguishable, except for one or two crucial phenomena to which reference will be made later. But in gravitational fields far stronger than any of which we have experi-

* The idea is that matter represents a seam or nucleus of strain, and the strains at other points link themselves on according to laws inherent in the *continuum* and quite independent of the matter. The matter starts the strain, but does not control it as it goes outwards.

ence, and for bodies moving with velocities much greater than those of the planets, the difference would be considerable.

This idea of the distortion of space as the *modus operandi* of gravitation has led to a practical result—a new law of gravitation. It is not brought in as a hypothetical explanation of gravitation; if Einstein's theory is true, it is simply of the nature of an experimental fact.

If we draw a circle on a sheet of paper and measure the ratio of the circumference to the diameter, the result gives, if the experiment is performed accurately enough, the well-known number π , which has been calculated to 707 places of decimals. Now place a heavy particle at or near the centre and repeat the experiment; the ratio will be not exactly equal to π , but a little more. The experiment has not been performed, and is not likely to be performed, because the difference to be looked for is so small; but, if Einstein's theory is correct, that must be the result. The space around the heavy particle does not obey ordinary geometry; it is non-Euclidean. The change in its properties is not metaphysical, but something which with sufficient care could be measured. You can keep to Euclidean space if you like, and say that the measuring-rod has contracted or expanded according as it is placed radially or transversely to the gravitational force. That is all very well if the effect is small, but in a very intense gravitational field it would lead to ridiculous results like those we noticed in connection with the Michelson-Morley experiment—everything expanding or contracting as it changed position, and no one aware of any change going on. I think we have learnt our lesson that it is better to be content with the space of experience, whether it turns out to be Euclidean or not, and to leave to the mathematician the transformation of the phenomena into a space with more ideal properties.

This consequence of the new law of gravitation, though theoretically observable, is not likely to be put to any practical test either now or in the immediate future. But there are other consequences which just come within the range of refined observation, and so give an immediate practical importance to the new theory, which has indeed scored one very striking success. If we could isolate the sun and a single planet, then under the Newtonian law of gravitation the planet would revolve in an ellipse, repeating the same orbit indefinitely. Under the new law this is not quite true; the orbit is nearly an ellipse, but it does not exactly close up, and in the next revolution the planet describes a new ellipse in a slightly advanced position. In other words, the elliptic orbit slowly turns round in the same direction in which the planet is moving, so that after the lapse of many centuries the orbit will point in a different direction. The rate at which the orbit turns depends on the speed of motion of the planet in its orbit, so we naturally turn to the fastest moving planets, Mercury, Venus and the Earth, to see if the

effect can be detected. Mercury moves at 30 miles a second ; Venus at 22 ; the Earth at 18½. But there is a difficulty about Venus and the Earth. Their orbits are nearly circular, and you cannot tell in which direction a circle is pointing. Mercury combines the favourable conditions of a high speed and a satisfactorily elongated orbit whose direction at any time can be measured with considerable precision. It is found by observation that the orbit of Mercury is advancing at the rate of 574 seconds of arc a century. This is in great measure due to the attraction of the other planets, which are pulling the orbit out of shape and changing its position. The amount of this influence can be calculated very accurately, and amounts to 532 seconds per century. There is thus a difference of 42 seconds a century unaccounted for ; and this has for long been known as one of the most celebrated discordances between observation and gravitational theory in astronomy. It is thirty times greater than the probable error which we should expect from uncertainties in the observations and theory. There are other puzzling discordances, especially in connection with the motion of the moon ; but the conditions in that case are more complicated, and I scarcely think they offer so direct a challenge to gravitational theory. Now Einstein's theory predicts that there will be a rotation of the orbit of Mercury additional to that produced by the action of the planets ; and it predicts the exact amount—namely, that in one revolution of the planet the orbit will advance by a fraction of a revolution equal to three times the square of the ratio of the velocity of the planet to the velocity of light. We can work that out, and we find that the advance should be 43 seconds a century—just about the amount required. Thus whilst the Newtonian law leaves a discordance of over 40 seconds, Einstein's law agrees with observation to within a second or so.

Of course this superiority would be discounted if we could find some other application where the old Newtonian law had proved the better. But that has not happened. In all other cases the two laws agree so nearly that it has not been possible to discriminate between them by observation. The new law corrects the old where the old failed, and refrains from spoiling any agreement that already exists. The next best chance of applying the new theory is in the advance of the orbit of Mars ; here Einstein's new law "gilds refined gold" by slightly improving an agreement which was already sufficiently good—a "wasteful and ridiculous excess" which is at any rate not unfavourable to the new theory.

There is another possibility of testing Einstein's theory, which it is hoped to carry out at the first opportunity. This relates to the action of gravitation on a ray of light. It is now known that electromagnetic energy possesses the property of inertia or mass, and probably the whole of the mass of ordinary matter is due to the electromagnetic energy which it contains. Light is a form of electromagnetic energy,

and therefore must have mass—a conclusion which has been found true experimentally, because light falling on any object exerts a pressure just as a jet of water would. We ordinarily measure mass in pounds, and it is quite proper to speak of “a pound of light,” just as we speak of a pound of tobacco. In case anyone should be thinking of going to an Electric Light Company to buy a pound of light, I had better warn you that it is a rather expensive commodity. They usually prefer to sell it by a mysterious measure of their own, called the Board of Trade Unit, and charge, at least, threepence a unit. At that rate I calculate that they would let you have a pound of light for £141,615,000. Fortunately, we get most of our light free of charge, and the sun showers down on the earth 160 tons daily. It is just as well we are not asked to pay for it.

But although light has mass, it does not follow that light has weight. Ordinarily, mass and weight are associated in a constant proportion, but whether this is so in the case of light can only be settled by experiment—by weighing light. It seems that it should be just possible to do this. If a beam of light passes an object which exerts a gravitational attraction, then, if it really has weight, it must drop a little towards the object. Its path will be bent just as the trajectory of a rifle bullet is curved owing to the weight of the bullet. The velocity of light is so great that there is only one body in the solar system powerful enough to make an appreciable bend in its path, namely, the sun. If we could see a star close up to the edge of the sun, a ray of light coming from the star would bend under its own weight, and the star would be seen slightly displaced from its true position. During a total eclipse stars have occasionally been photographed fairly close to the sun, and with care it should be possible to observe this effect. There is a magnificent opportunity next year when a total eclipse of the sun takes place right in the midst of a field of bright stars. This is the best opportunity for some generations, and it is hoped to send out expeditions to the line of totality to weigh light according to this method.

In any case great interest must attach to an attempt to settle whether or not light has weight. But there is an additional importance, because it can be made a means of confirming or disproving Einstein's theory. On Einstein's theory light must certainly have weight, because mass and weight are viewed by it as two aspects of the same thing; but his theory predicts a deflection twice as great as we should otherwise expect. Apart from surprises, there seem to be three possible results: (1) a deflection amounting to $1.75''$ at the limb of the sun, which would confirm Einstein's theory; (2) a deflection of $0.83''$ at the limb of the sun, which would overthrow Einstein's theory, but would establish that light was subject to gravity; (3) no deflection, which would show that light though possessing mass has no weight, and hence that Newton's law of proportionality between mass and gravitation has broken down in another unexpected direction.

The purpose of Einstein's new theory has often been misunderstood, and it has been criticized as an attempt to explain gravitation. The theory does *not* offer any explanation of gravitation; that lies quite outside its scope, and it does not even hint at a possible mechanism. It is true that we have introduced a definite hypothesis as to the relation between gravitation and a distortion of space; but if that explains anything, it explains not gravitation but space, i.e. the scaffolding constructed from our measures. Perhaps the position reached may be made clearer by another analogy. Let us picture the particle which describes a world-line as hurdle-racer in a field thickly strewn with hurdles. The particle in passing from point to point always takes the path of least effort, crossing the fewest possible hurdles; if the hurdles are uniformly distributed, corresponding to undistorted Minkowskian space, this will, of course, be a straight line. If the field is now distorted by a mathematical transformation such as an earthquake so that the hurdles become packed in some parts and spread out in others, the path of least effort will no longer be a straight line; but it is not difficult to see that it passes over precisely the same hurdles as before, only in their new positions. The gravitational field due to a particle corresponds to a more fundamental rearrangement of the hurdles, as though someone had taken them up and replanted them according to a law which expresses the law of gravitation. Any other particle passing through this part of the field follows the guiding rule of least effort, and curves its path if necessary so as to jump the fewest hurdles. Now, we have usually been under the impression that when we measured distances by physical experiments we were surveying the *field*, and the results could be plotted on a map; but it is now realized that we cannot do that. The field itself has nothing to do with our measurements; all we do is to count hurdles. If the only cause of irregularity of the hurdles were earthquakes (mathematical transformations) that would not make much difference, because we could still plot our counts of hurdles consistently as distances on a map; and the map would represent the original condition of the field with the hurdles uniformly spaced. But the more far-reaching rearrangement of hurdles by the gravitational field forces us to recognize that we are dealing with counts of hurdles and not with distances; because if we plot our measures on a map they will not close up. The number of hurdles in the circumference of a circle* will not be π times the number in the diameter; and when we try to draw on a map a circle whose circumference is more than π times its diameter, we get into difficulties—at least in Euclidean space. This

* A circle would naturally be defined as a curve such that the number of hurdles (counted along the path of least effort) between any point on it and a fixed point called the centre is constant. To make the vague analogy more definite, we may suppose that the hurdles are pivoted, and swing round automatically to face the jumper; he is not allowed to dodge them, i.e. to introduce into his path sinuosities comparable with the lengths of the hurdles.

analogy brings out the point that the theory is an explanation of the real nature of our measures rather than of gravitation. We offer no explanation why the particle always takes the path of least effort—perhaps, if we may judge by our own feelings, that is so natural as to require no explanation. More seriously, we know that in consequence of the undulatory theory of light, a ray traversing a heterogeneous medium always takes the path of least time; and one can scarcely resist a vague impression that the course of a material particle may be the ray of an undulation in five dimensions. What concerns gravitation more especially is that we have offered no explanation of the linkages by which the hurdles rearrange themselves on a definite plan when disturbed by the presence of a gravitating particle; that is a point on which a mechanical theory of gravitation ought to throw light.

From the constant of gravitation, together with the other fundamental constants of nature—the velocity of light and the quantum of action—it is possible to form a new fundamental unit of length. This unit is 7×10^{-24} centimetres. It seems to be inevitable that this length must play some fundamental part in any complete interpretation of gravitation. (For example, in Osborne Reynold's theory of matter this length appears as the mean free-path of the granules of his medium.) In recent years great progress has been made in knowledge of the excessively minute; but until we can appreciate details of structure down to the quadrillionth or quintillionth of a centimetre, the most sublime of all the forces of nature remains outside the purview of the theories of physics.

[A. S. E.]

APPENDIX.

OUTLINE OF THE MATHEMATICAL THEORY OF EINSTEIN'S LAW OF GRAVITATION.

The fundamental formula, by which from measurements we infer the relative positions of objects in a space defined by three rectangular co-ordinates, x , y , z , is—

$$ds^2 = dx^2 + dy^2 + dz^2 \quad (1)$$

where ds is the *measured* element of length, and the right-hand side refers to the *inferred* positions. Experiments are concerned with fields of gravitation which from the present point of view must be regarded as extremely weak, so the formula must be taken as applying strictly only in the absence of gravitation. (We have no proof that in a strong gravitational field the formula would be self-consistent, i.e. that measured space would be Euclidean.)

In four dimensions, the formula is generalized to—

$$ds^2 = dx^2 + dy^2 + dz^2 - dt^2 \quad (2)^*$$

Here, again, ds is a measured quantity (partly by scales and partly by clocks), and the right-hand side refers to the inferred locations. The units are chosen so that the velocity of light is unity. According to the old theory of relativity the measured "distance," ds , between two events is not affected by any uniform motion of the observer.

If four new co-ordinates x_1, x_2, x_3, x_4 , which are arbitrary functions of x, y, z and t , are introduced and substituted in the right-hand side of (2), we obtain an equation of the general form—

$$ds^2 - g_{11} dx_1^2 + g_{22} dx_2^2 + \dots + 2g_{12} dx_1 dx_2 + 2g_{13} dx_1 dx_3 + \dots \quad (3)$$

where the g 's are functions of the co-ordinates. Cubes and higher powers of the infinitesimals can be neglected.

In natural rectangular co-ordinates the path of a particle under no forces is a straight line described with uniform velocity, or more briefly a straight line in four dimensions. This may be expressed in a form which is independent of the choice of co-ordinates, viz. $\int ds$ is a minimum. By substituting under the integral the value of ds from (3) and applying the calculus of variations, we obtain the general equations of motion under no forces applicable to any system of co-ordinates. The g 's and their derivatives will occur in these equations.

In particular, by taking x_1, x_2, x_3, x_4 to be rectangular axes rotating with the earth, we should obtain the equations of motion of a particle under no "real" forces referred to those axes—in other words, the equations of motion of a particle in a field of centrifugal force. The centrifugal force enters into the equations through the intermediary of the corresponding g 's; and we thus get the notion of a field of force as defined by a set of values of the g 's. Our hypothesis of the complete equivalence of gravitation to forces like the centrifugal force arising from a transformation of the axes of reference shows that we may also define the gravitational field by a set of values of the g 's. In the case of the centrifugal force the values of the g 's are such that by a transformation of the co-ordinates we can transform (3) to (2). It does not necessarily follow that this can be done when the g 's have values corresponding to a gravitational field; and in fact we cannot do it for a *finite* region of space, although, of course, in an infinitesimal element gravitation may be made to disappear by an appropriate transformation.

The g 's defining the gravitational field may be regarded as the ten components of a generalized gravitational potential. In fact, in rectangular co-ordinates one of them, g_{11} , corresponds to twice the Newtonian potential.† Newton's law is therefore expressed by Laplace's equation—

$$\nabla^2 g_{11} = 0 \quad (4)$$

in free space. It is impossible to accept this as a general law satisfied by the g 's, because, for example, it is not satisfied when the g 's repre-

* This formula is usually given with the reversed sign.

† It is an easy illustration to work out the transformation of (2) to rotating axes, when it will be found that g_{11} is twice the potential of the corresponding centrifugal force.

sent a centrifugal force. Clearly the hypothesis of equivalence requires that there should be one or more general differential equations satisfied by the g 's in all cases, and not a special law satisfied by gravitational g 's and another satisfied by distortion g 's. If, then, the law is a general relation between the g 's, it must hold for all systems of co-ordinates; that is, it must be co-variant for all transformations.

The general condition satisfied by the g 's in the absence of a gravitational field is written in the form—

$$B'_{\mu\sigma\tau} = 0 \quad (5)$$

where the quantity on the left is known as the Riemann-Christoffel tensor. (The word *tensor* expresses the property, that if it vanishes in one system of co-ordinates it vanishes in all systems.) It is a function of the g 's and their first and second derivatives with respect to x_1, x_2, x_3, x_4 . It has 256 components, formed by ringing the changes on the suffixes ρ, μ, σ, τ , giving them the values 1, 2, 3, 4.* By symmetry many of these are identical, and we actually get (I think) 96 apparently different equations, some of which may not be independent. The equation (5) is to be understood to mean that all the 96 components vanish. The equation expresses the fact that a mathematical transformation exists which can transform (3) to (2) throughout space; and that is the method by which it is obtained analytically.

The general equation between the g 's, allowing for a gravitational field, must be less stringent; it must be such that it is satisfied when (5) is satisfied, but not necessarily *vice versa*. (Zero gravitation is a particular case of gravitation, but not *vice versa*.) The simplest symmetrical law that we could propose is—

$$B_{\mu\sigma} - \sum_{\rho=1}^4 B^{\rho}_{\mu\sigma\rho} = 0 \quad (6)$$

This is clearly satisfied when (5) is satisfied.

$B_{\mu\sigma}$ is called the reduced (*verjüngt*) Riemann-Christoffel tensor, and has ten different (but not all independent) components. It seems to be the only possible way of symmetrically building up another tensor out of the components of $B^{\rho}_{\mu\sigma\tau}$; and it appears also that equation (6) is the only co-variant equation of the second rank (i.e., having ten components) that can be formed from the g 's, and their first and second derivatives and linear in the last. Co-variant equations of higher rank (with more components) would impose too great restrictions, and like the Riemann-Christoffel tensor would not admit a gravitational field.

For this reason (6) is chosen as the new law of gravitation. It reduces to the Newtonian law as first approximation.

It remains to see how the equation (6) is modified when the space is occupied by mass, i.e. electromagnetic energy. What is to be

* It would be cumbersome to write down the value of $B^{\rho}_{\mu\sigma\tau}$; but it will be understood that it contains $g_{\mu\sigma}, x_{\rho}$, etc., and the different components are got by giving the values 1, 2, 3, 4 to the suffixes.

the new form of Poisson's equation $\nabla^2\phi = -4\pi\rho$? It is found that equation (6) can be transformed into a Hamiltonian form—

$$\delta(\int H d\tau) = 0 \quad (7)$$

where $d\tau$ is a four-dimensional element of volume, and H a certain function of the g 's and their derivatives.

The electromagnetic equations of Maxwell in the absence of a gravitational field can also be expressed in a Hamiltonian form—

$$\delta(\int H' d\tau) = 0 \quad (8)$$

where H' is a function of the quantities defining the electromagnetic field.

It is clear that we must form the general equations, when gravitation and electromagnetic forces are both present, by combining (7) and (8) thus—

$$\delta(\int (H + \lambda H') d\tau) = 0 \quad (9)$$

The constant λ , whose value cannot be predicted *a priori*, indicates the relation between the gravitational and electromagnetic effects caused by the same mass, and corresponds to the constant of gravitation.

The mathematical operations, omitted in this brief sketch, are long and rather difficult; but it is hoped that it may enable the reader to gather the general nature of the argument.

Friday, March 8, 1918.

THE RIGHT HON. LORD RAYLEIGH, O.M. LL.D. D.Sc. F.R.S.,
in the Chair.

PROFESSOR EDWIN H. BARTON, D.Sc. F.R.S.

Vibrations: Mechanical, Musical, and Electrical.

I.—INTRODUCTORY SURVEY.

THE subject of vibrations is a large one. It comprises a great variety of to-and-fro motions, and these may be executed by diverse systems at widely differing rates. Near one border of the subject lie phenomena so simple that a child may grasp their leading features. Near the opposite border there are phenomena of exceeding complexity and their full solution is still awaited.

It thus appears that parts of the subject are too elementary and familiar for detailed treatment here, while others may be not yet ripe for general description. But between these extremes there are portions or aspects of the subject that may prove both interesting and practicable.

To indicate and locate a few such portions a brief survey of the subject was then taken. Many ways of classifying vibrations are available. But, without aiming at logical precision, a somewhat rough method was considered convenient. Thus, since a vibration is a to-and-fro motion, the various types of such motions may be placed in columns. Secondly, since these motions are executed by some physical systems, the various systems may be placed in rows or lines. This gives the sub-division shown in Table I.

Neither the columns nor the rows need stop just where they do in this table. For the subject extends further in each direction. Moreover, each column and row admits of further sub-division. So that the ramifications of the subject are almost beyond enumeration. But, as it is, it serves to locate the portions to which chief attention was directed. These were examples of two or more associated vibrations whether forced, coupled or compound.

II.—FORCED AND COUPLED VIBRATIONS.

Forced and *coupled* vibrations must be distinguished from each other and from the simplest class of all called *free* vibrations. To

do this pass along the first row in Table I. taking the cases of the pendulums there shown.

If a pendulum bob is pulled aside and let go, it returns towards its zero position under the combined effect of gravity and its slant suspension. On reaching the zero position with a certain velocity it overshoots the mark because the bob has inertia. Thus a free vibration is set up. This may continue until slowly extinguished by friction which is operating all the time to diminish the swings. Next let the point of suspension of a pendulum be moved slightly to-and-fro by periodic forces. Then the pendulum would be set in

TYPICAL VIBRATIONS



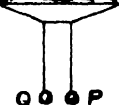
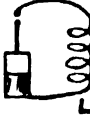
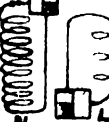
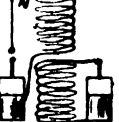


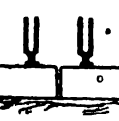
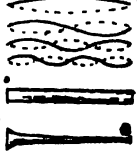
MOTION SYSTEMS	FREE	FORCED	COUPLED	COMPOUND
MECHANICAL				
ELECTRICAL				
MUSICAL				

TABLE I.

vibration and kept going. Further, the motions would settle down to a quite definite amplitude and phase. These are the *forced vibrations*. Their amplitude would depend upon that of the point of suspension and also on the *tuning*. By tuning is meant the degree of agreement between the period natural to the pendulum and that of the forces applied to it. The closer the tuning between them the better the response. Upon the tuning depends also the *phase* of the forced vibrations. When the forces alternate appreciably slower than the vibrations natural to the pendulum the two are almost in like

phases. But when the forces alternate quicker than the pendulum, the latter swings almost in opposite phase.

This change of phase of forced vibrations was illustrated by three hanging pendulums all hanging from the same tightly stretched horizontal cord. One pendulum had a heavy bob and by its swings moved the stretched cord. It thus acted as *driver* and applied forces to the other two pendulums which had light bobs and so were easily *driven*. Of these pendulums one was shorter and one longer than the driver. They soon settled to opposite phases after the heavy bob was set in motion. *Resonance* curves showing the varied responses of such driven pendulums as the tuning is altered were then shown on the screen.

In the cases just dealt with the light bob is set in motion at the expense of energy taken from the heavy one. But on account of the great disparity of the bobs this loss entailed no appreciable diminution in the vibrations of the heavy bob or driver.

Consideration was next given to the case where equal bobs hang from a tight cord. While both pendulums are hanging at rest one bob is struck. Its vibrations disturb the other pendulum and set it in motion. But obviously, while the driven pendulum gains an amplitude equal to that first possessed by the driver, the driver itself would have lost all its motion. The other then becomes the driver in turn and transfers its energy back to what was originally the driver. (Demonstration).

This palpable surging of the energy to and fro between the two pendulums marks them as showing what may be called *coupled* vibrations. In both cases the action of the driver on the driven is recognised. But in the case of coupled vibrations the *reaction* of the driven on the driver is palpable and recognised also. Whereas in what are called forced vibrations this reaction is undiscernible or ignored.

In the case of coupled vibrations just shown the vibrations of each pendulum seem quite simple, but slowly and alternately wax and wane in amplitude, that is, they exhibit what are termed "*beats*." But it is well known that beats may be heard when two musical tones of slightly differing pitch are sounded together. Further, the number of beats per second is the difference of the frequencies of the two tones. Thus the waxing and waning vibrations of either pendulum may be regarded as the superposition of *two* simple vibrations of slightly different periods.

The next case studied was that of two precisely similar pendulums connected by hanging one from the bob of the other. One bob being started by a blow it appeared to execute simple vibrations. The other moved with a pause or twitch instead of in simple fashion. Further, neither pendulum showed the waxing and waning of amplitude which was so marked in the other case where both hung from a stretched cord.

The questions which now naturally arise are (*a*) why this contrast? and (*b*) can the gap be bridged? The solution is simple. The difference in appearance is only a matter of different ratios of periods of the superposed vibrations. And this again is due to different values of the *coupling*, to borrow a term from electrical theory. We have changed suddenly from a very loose to a very tight coupling. We consequently passed at a bound from periods nearly equal (giving a slow waxing and waning) to periods whose ratio exceeds 2:1 (involving the pause or twitch); for the theory shows that as the coupling increases the ratio of the periods increases also.

It is accordingly of interest to change the coupling gradually and so bridge the gap between the two motions which seemed so unlike. This was done by the cord and lath pendulum, in which the cord pendulum is suspended from an adjustable stud on the lath pendulum. When the two suspensions are near together the value of the coupling is almost equal to the fraction of the lath length at which the cord is attached. When this fraction is unity, as in the case of one pendulum hanging from the bob of the other, the coupling has the value $1/\sqrt{3}$ or 58 per cent. nearly. (These simple relations are for equal bobs and equal pendulum lengths.)

III.—ELECTRICAL VIBRATIONS, FORCED AND COUPLED.

On passing along the second line of Table I., it was noted how the various types of electrical vibrations may be obtained and the striking analogy to them presented by the mechanical cases already considered.

Any electrical circuit containing a capacity and an inductance may exhibit electrical vibrations. For the fundamental electrical conditions are there present just as the mechanical ones were in the case of a simple pendulum. If the condenser is charged by a suitable means, the quantity of electricity so displaced is urged to flow back again round the circuit by the electromotive force of the charged condenser. If the resistance of the circuit is small enough the electromagnetic inertia (measured by the inductance) ensures that the current shall still flow after the condenser is discharged. Thus its charge is reversed. So the vibrations continue till the energy is dissipated by the resistance of the circuit. These are *free* electrical vibrations.

As an example of forced electrical vibrations we may think of a circuit with capacity and small inductance (like that of a Fleming cymometer), placed not too near to a circuit of similar frequency but with much greater inductance. Then the cymometer will respond to the vibrations of the other, i.e. it will execute *forced* vibrations. These will not appreciably diminish the vibrations of the main circuit.

But let two electrical vibration circuits of comparable inductances and periods be placed together and started, then there is not only the action of the driver but also a distinct *reaction* of the driven on the driver. Hence, as the vibrations of one circuit start those of the other, the latter by their growth check the former, causing them to die away. Thus there may be an interchange of energy between them. This, as we have seen with pendulums, corresponds to the superposition of vibrations of slightly differing periods, provided the action and reaction are small and the interchange slow. Further, it is known that if two such circuits are closely coupled those two periods differ more widely. Hence a third circuit (say a cymometer) responding to either of them may detect these separate periods by giving a resonance curve with two humps instead of one.

IV.—TRACES FROM COUPLED PENDULUMS.

It has been seen that there is a certain general analogy between mechanical and electrical vibrations, whether free, forced or coupled. The question now arises as to whether this analogy may reach or approach a quantitative exactness in all or any respect, and whether it can be utilised in any way.

Various mechanical vibrating systems differ widely. Some resemble the electrical case very closely, but none appears to be completely and exactly analogous to them in every detail. Indeed the electrical case seems to be slightly simpler than any mechanical analogy yet put forward. But the differences are small, and the mechanical analogy may be highly useful as affording visible and tangible illustrations of those subtle electrical vibrations which can be neither seen nor handled. Especially is this the case if the model is readily adjustable to represent the various relations of the constants concerned and can be used for any initial conditions. Thus from such analogies some benefit may accrue to the non-mathematical student. But perhaps the highest advantage is realised only by those who combine the mathematical with the experimental study and grope after the ideal model which shall represent exactly the electrical or other phenomena in question. But whatever the uses of such models, certain it is that their design and study have exercised a fascination on many eminent scientists. In this connection it may suffice to mention Faraday, Maxwell, Lord Kelvin, Lord Rayleigh, Sir Oliver Lodge, Sir Joseph Thomson, Professors J. A. Fleming, T. R. Lyle, and W. S. Franklin.

For either quantitative work or mere illustration the usefulness of such a model is much enhanced if its vibrations leave traces. This is easily arranged by letting the bobs carry funnels of sand under which a blackboard moves uniformly at right angles to the direction of vibration. In the portable apparatus shown in Fig. 1 the

pendulums are of the double-cord type and allow both traces to be obtained simultaneously, and thus record the relations of amplitude and phase for each pendulum. With this apparatus the coupling can be varied at will and easily adjusted to any desired value from 1 per cent. to 60 or more. The greater the droop of the bridles the greater the coupling, the quantitative relation being simple. It is noteworthy that, for equal bobs and pendulum lengths, a 60 per cent. coupling gives superposed periods as 2:1, just as in the electrical case for equal periods. Indeed, with any specified coupling, the

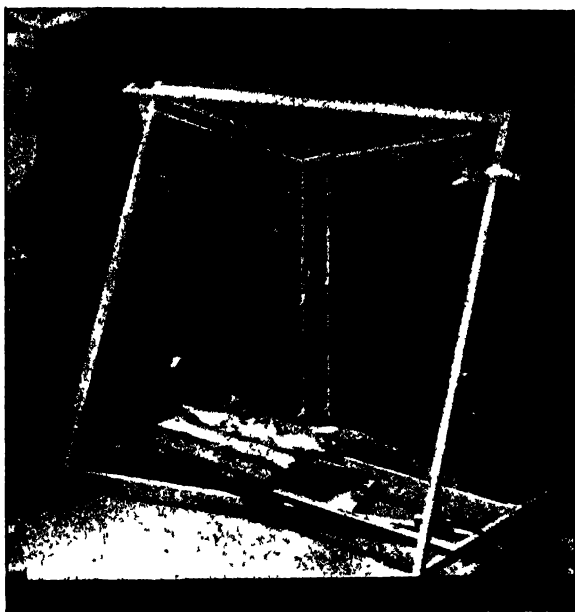


FIG. 1.—COUPLED PENDULUMS

ratio of periods is the same for this mechanical case and for the electrical one. The masses of the bobs and the lengths of the pendulums are adjusted at pleasure, and the initial conditions may be anything that is desired. (Simultaneous traces with this apparatus were then obtained, others exhibited, and photographs of a number thrown on the screen.)

With equal bobs and equal lengths, the coupling being small, each pendulum exhibits in turn the same maximum and the same minimum as the other. With small couplings, equal lengths, but bobs as 20:1, the case of forced vibrations is approached. That is

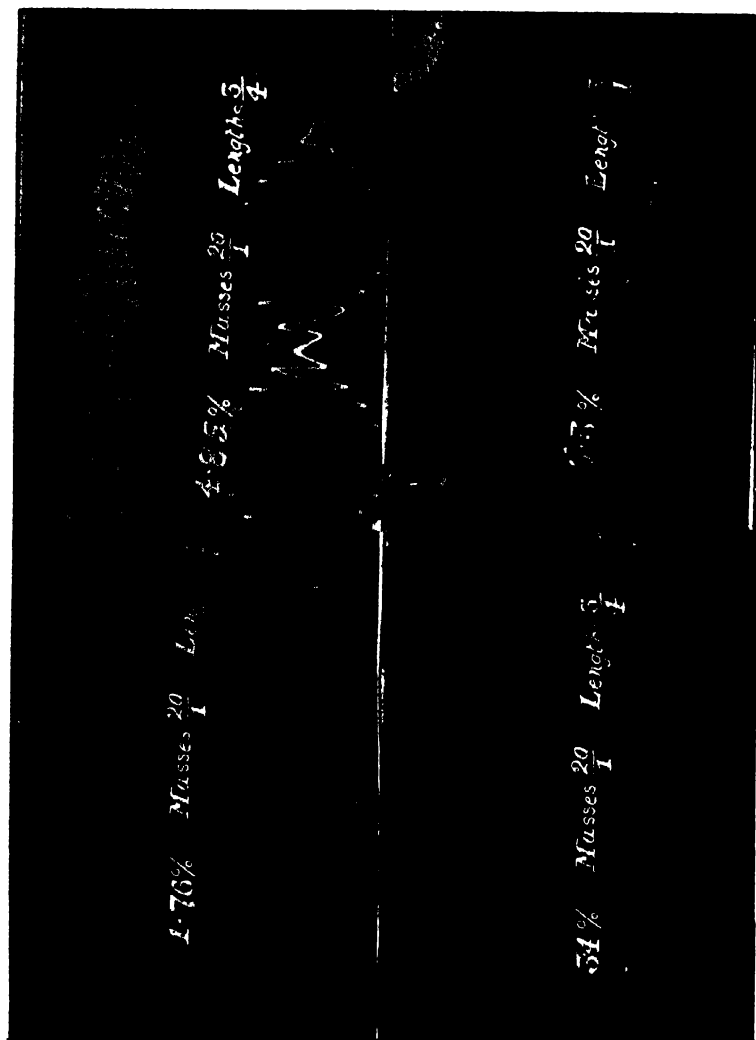


FIG. 2.—VIBRATION TRACES OF COUPLED PENDULUMS.

to say, the heavy bob loses but little amplitude, while that of the light bob grows from zero to its maximum. With bobs as 5 : 1, the heavy bob loses appreciably, while the light one proceeds to its maximum.

As the coupling increases from zero the ratio of the periods of the superposed vibrations of the coupled pendulums usually increases continuously till it equals or exceeds 2 : 1. When, however, both lengths and masses are unequal, the *short* length having the *heavy* bob, a new feature appears. As the coupling gradually increases from zero, the ratio of the periods at first diminishes, reaches a *minimum*, and then increases. Thus the number of vibrations in a beat cycle at first increases, reaches a *maximum*, and then decreases. These special effects are shown in Fig. 2. They were theoretically predicted and then experimentally confirmed. The maximum number of vibrations in the beat cycle occurs for the highest coupling shown in the figure, viz. 6·3 per cent. The details as to bobs, lengths and couplings are all indicated on the figure. The able collaboration of Miss H. M. Browning in this work was gratefully acknowledged.

V.—BRASS INSTRUMENTS AND THE LOW "F."

Leaving the pendulums which have only two vibrations at a time, the case of brass instruments with a number of simultaneous vibrations was next considered. It is well known that the vibrations from most musical instruments are what is called compound. They consist of a series of tones of commensurate frequencies sounded together. Thus, if the pitch of the note is said to be 100 per second, there is not only a prime tone of this frequency, but also a second tone of 200 per second, a third of 300 per second, and so forth. This law applies to strings, to open parallel pipes, and to a complete cone with its base open. It also applies as a close approximation to the brass instruments in general use. This approximation is traceable to the departure from the strictly conical form as regards the mouthpiece, the bell, and the special shape of the intermediate portion.

In these brass instruments the possibility of this compound tone, or multiple resonance, is utilised for the production of distinct notes. Thus, out of the tones possible to the instrument the player may elicit the set 200, 400, 600, 800, etc.; or the set 300, 600, 900, 1200, etc. These would be said to have the pitches of their primes, or lowest components 200 or 300 respectively. Or, to put it musically, they would be the octave or the twelfth of the fundamental (or pedal) possible on the instrument. The pedal of the instrument is not usually employed for musical purposes, but can be sounded if specially wished. Now, there is a tradition among players of brass

instruments that a note called by them a low "F" can be sometimes obtained. This note would have on the foregoing scheme the frequency $133\frac{1}{3}$. At first the possibility of this "F" seems scarcely credible to the theoretician. But after hearing and producing the note, the necessity of accounting for its possibility was forced home.

And really the explanation proves very simple. It usually depends upon two points; (a) the *spread or diffused resonance* of of the pedal; and (b) its intentional *mistuning* with respect to the other notes of the instrument. These are taken in order.

(a) For theory shows that, other things being equal, the lower the note of such an instrument, the easier it is to force its vibrations out of tune, sharper or flatter. Thus, with the pedal the range of

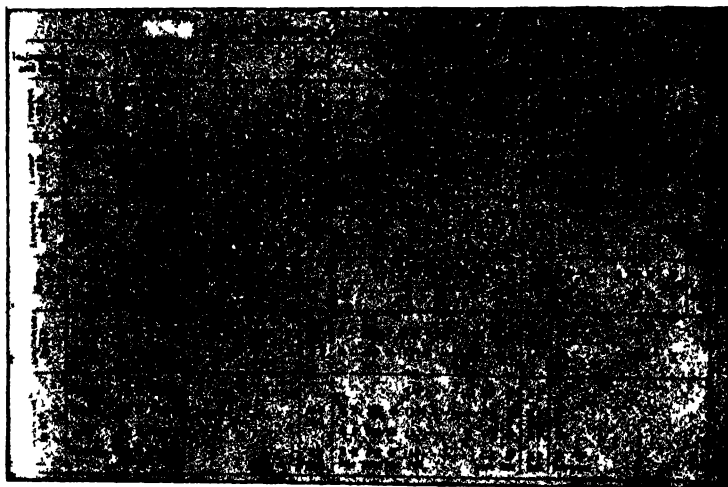


TABLE II.—Spread Resonance of Lower Open Notes on Brass Instruments

resonance is such that the note may be sounded at any pitch whatever over a range of five or six semitones.

(b) Since the law of frequencies 100, 200, 300, 400, etc., is only approximately true for these instruments, in order to secure good relative tuning of the higher notes which are in constant use the pedal (which is not used musically) is purposely mistuned. On some instruments it may be say, D or E flat, instead of C.

Hence, if the central pitch of the pedal is sharpened two or three semitones, and it is possible to force this note both up and down two or three semitones, it becomes possible to sound the pedal of true pitch C, to sound the low "F," and to sound notes of every

pitch between. (This was demonstrated on a euphonion kindly lent by Messrs. Boosey & Co.)

The low "F" is also possible on the bombardon. Both these instruments are characterised by large conical tubing, and the low "F" is obtained by the spread resonance of the sharpened pedal.

In the case of the trumpet, cornet and French horn with much narrow tubing, the pedals are flattened, so that a pedal of true pitch can only be obtained by the spread resonance, and the "F" is impossible. On the trombone, which has much small parallel tubing, the low "F" may be obtained occasionally by the downward spread resonance of the second partial (or note number two), which is an octave above the pedal. (Demonstration.) The pitch of the notes which have been obtained on six types of instruments by four experimenters are shown in Table II.

VI.—MONOCHORD VIBRATIONS.

Consideration was next given to the vibrations of stringed instruments, beginning with the monochord, because of its striking simplicity.

From the work of mathematicians (with a little help from experiment) the various possible vibrations of strings, whether plucked, struck or bowed, have long been well known. But a little reflection will show that many other problems are still left confronting the physicist. For identical strings excited in the same way, but mounted on different instruments, will produce very different effects on the ear. In other words, the worth of a violin does not lie in its strings, but in its sound-box.

This leads to the inquiry as to what happens to modify the vibrations as, passing from the strings, they reach in turn the bridge, the belly (or sound-board) and the adjacent air.

It is easy to see that this problem is somewhat complicated, since it presents so large a number of variables. Thus, there lie at the experimenter's disposal the pitch of the string, its material and dimensions, the place and manner of excitation, the material and disposition of the associated parts of the instrument, the place of observing the belly, the portion of the bridge observed and the directions of its motions, and, lastly, the spot at which the motion of the air is observed. In this way a scheme for over a thousand observations could be sketched, even for an instrument with but one string.

Hence no exhaustive treatment of the problem can be quickly obtained. But a beginning has been made, and by very simple means.

In a series of experiments simultaneous records have been photographically obtained of the vibrations of the string and of some other part of the instrument. The monochord was placed on a table and light from a vertical slit was focused upon the string near

its centre. The real image of this slit, crossed by the shadow of the string, was then focused by a second lens on to a photographic plate in a dark room. This plate was shot along horizontal rails by elastic cords which were just slack when the plate received the light. Thus the plate moved uniformly and horizontally, while the shadow of the vibrating string showed its special motion vertically. The corresponding motions of bridge, belly, or air were obtained on the same photographic plate by the light reflected from a tiny rocking mirror

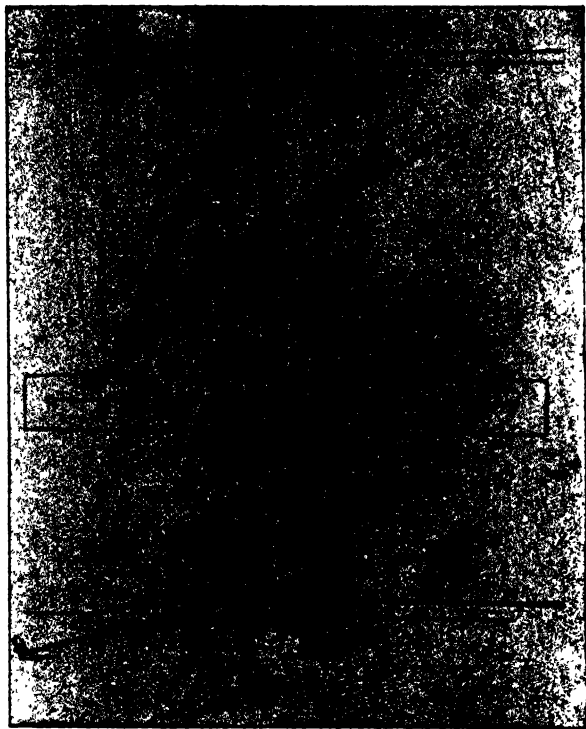


FIG. 3.—MONOCHORD APPARATUS.

whose slight tilt was produced by the motion of the part under test. (The principle of this experimental method was then demonstrated, the humped form of the curve due to plucking the string and the two-step zig-zag produced by careful bowing being shown.) Fig. 3 gives a diagram of the method for the monochord, also a detail of the rocking mirror for the bridge's motion. Fig. 4 shows photographic traces for the monochord string and belly. The two curves

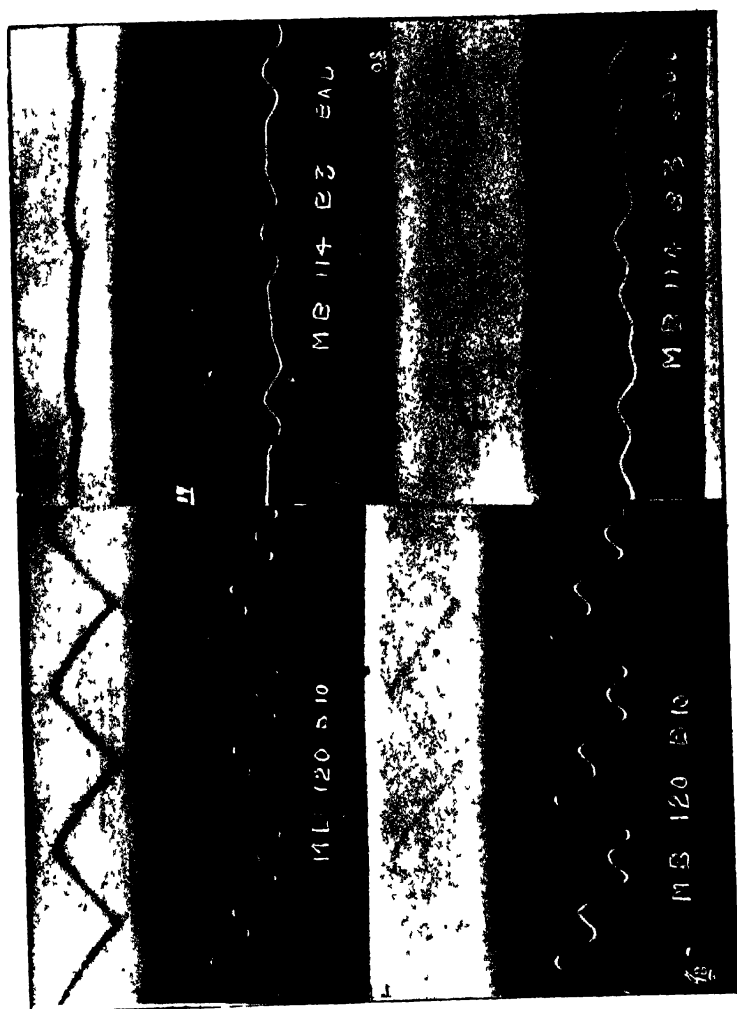


FIG. 4.—MONOCHORD VIBRATION CURVES.

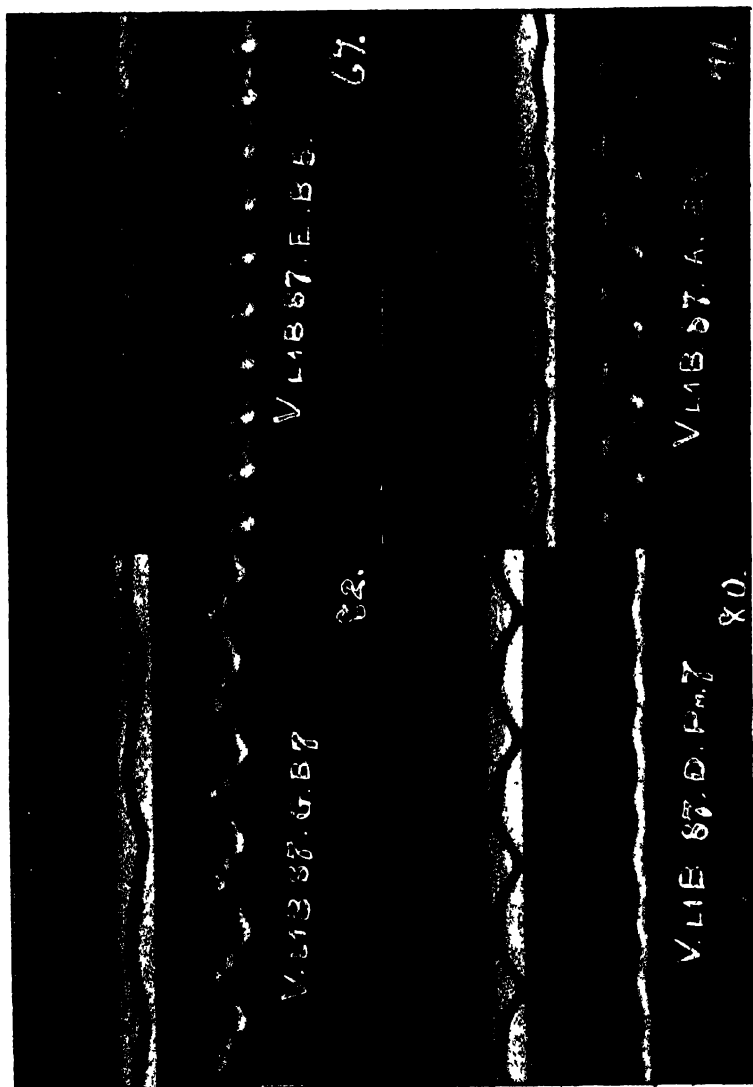


FIG. 5.—VIOLIN VIBRATION CURVES.

alike were taken separately to test if the apparatus worked satisfactorily. The other two curves, slightly different from each other, show the distinction in appearance between the records of a bad tone and a good one.

In this work the assistance of Messrs. C. A. B. Garrett and J. Penzer was acknowledged. In 1914 Prof. C. V. Raman, of Calcutta, by experiments somewhat similar to the above, showed that the forward speed of a string where it is bowed is identical with that of the bow itself.

VII.—VIOLIN VIBRATIONS.

If the problems of the monochord were numerous and complicated, those of the violin are still more so. For there are now four strings instead of one; further, all are different in thickness and pitch, and are capable of use in sections of varying length. Again, the sound-box is curved in a variety of ways. Finally, the reinforcement of the belly is asymmetrical. The bass bar lies almost under the fourth string, while the sound-post stands near that foot of the bridge which is under the first string. In the work on the violin assistance was received from Messrs. T. J. Richmond, T. F. Ebbelwhite, and W. B. Kilby. A number of vibration curves obtained for the violin were shown on the screen. Fig. 5 gives one set of these, showing the vibrations of each string as indicated by the letters G, D, A and E. The D string was plucked by a sharp point, the other strings were bowed. The white line shows the longitudinal motions of that corner of the bridge near which the first, or E, string passes.

VIII.—CONCLUSION.

With respect to the sympathetic vibrations occurring in stringed instruments, it is obvious that though a little has been done much more remains awaiting attack. Thus, the violoncello, guitar and harp might be dealt with. But specially, because of its immense vogue, the pianoforte needs thorough investigation. A start was made some time ago by Mr. G. H. Berry, and further researches are now in progress in London under the joint direction of scientists and piano manufacturers.

In the past music lovers and scientists alike have been deeply indebted to the makers of musical instruments, who have themselves received but little help from science in return. The lecturer expressed the hope that science might shortly pay off part of its debt to the musical craftsmen of the country and help to make the British piano second to none in the world.

[E. H. B.]

Friday, February 28, 1919.

THE RIGHT HON. LORD WRENBURY, P.C. M.A.,
Vice-President, in the Chair.

SIR OLIVER J. LODGE, D.Sc. LL.D. F.R.S. M.R.I.

**Ether and Matter: Being Remarks on Inertia, and on
Radiation, and on the possible Structure of Atoms.**

[AMPLIFIED FROM THE LECTURE.]

PART I.—INERTIA.

WE are each of us flying through space at nineteen miles a second, probably much more. Nothing is propelling us; we continue to move by our own inertia, simply because there is nothing to stop us. Motion is a fundamental property of matter. No piece of matter is at rest in the ether, the chances are infinite against any piece having the particular velocity zero; every bit is moving steadily at some given speed, unless acted on by unbalanced force. Then it is accelerated—changed either in speed or direction, or both.

As a matter of fact we, like other bodies on the earth, are acted on by two slight unbalanced forces—one which makes ~~us~~ revolve round the earth once a day, like a satellite, the other which makes us revolve round the sun once a year, like a planet or asteroid. Our annual revolution is not because we are attached to the earth; we are not attached, but revolve as independent bodies, and would revolve in just the same time and way if the earth were suddenly obliterated: only then we should find the diurnal revolution transmuted into a twenty-four hour rotation round our own centres of gravity, and the excentricity of our annual orbit very slightly changed. In any case there is no propelling force, only a residual radial force producing curvature of path.

A railway train, or a ship moving steadily, is likewise subject to no resultant force. Propulsion and resistance balance. The whole power of an engine, after the start, is spent in overcoming friction. The motion continues solely by inertia. Any steadily moving body is an example of the first law of motion. You need not try to think of a body under no force at all; you cannot think of such a body on the earth, but you can think of one under no resultant force, i.e. under balanced forces. Such a body moves by reason of its inertia alone. It is in equilibrium: it is not at rest.

But we have no sense of straightforward locomotion, and not the slightest clue to either the magnitude or direction of our motion through space. We can ascertain approximately how the sun is moving with reference to our system or cosmos of stars, but we do not know at what rate that system is itself moving. For all we know it may be moving very fast: hundreds of miles per second.

We have a sense of acceleration however; we experience it in a lift as it begins to descend; and if the sensation is repeated often enough, as on a rough sea, the result is unpleasant. We have also a sense of rotation; we can tell when our vehicle—say a Tube train—turns a corner in the dark. Most animals appear to have a sense of rotation, apparently located in the ear. But we have no sense of direct translation; and we have so far failed to devise any instrumental means for detecting our motion through the ether of space.

The failure is not for lack of trying. Many experiments have been tried, but there is always some compensating effect; so we get no answer to the question—at what rate and in what direction are we moving? The best known experiment is that of Michelson and Morley, the result of which seems to assert that the ether clings to the earth, or that the earth is not moving through any kind of substance. But FitzGerald's classical experiment showed that a transparent body carried with it none of the internal ether of space; and experiments made by myself* at Liverpool in the nineties of last century show that a rapidly moving opaque body carries no external ether with it, that there is no perceptible viscous drag or cling between matter and ether, and accordingly demonstrates that stagnation or absence of relative ether drift past the earth is not a reasonable explanation of Michelson's negative result.

The two experiments together, in fact, ought to be taken as establishing the reality of the most interesting of all the compensating effects yet discovered, viz. the FitzGerald-Lorentz contraction of all matter in motion, which the electrical theory of cohesion renders so extremely probable. It only amounts to a 3-inch shrinkage in the whole diameter of the earth in the direction of motion; but it is enough. This slight contraction or change of shape in moving bodies I regard as the definite and interesting compensating effect in this case. Incidentally, moreover, it establishes the electrical, i.e. the chemical, nature of cohesion. For given that cohesion is a residual chemical affinity—due to the outstanding attraction of molecules composed of neutral groups of equal opposite electric charges, brought so near together that the attraction between molecules is no longer averaged to zero†—then, on orthodox Maxwellian electric theory, a

* See Phil. Trans., vol. clxxxiv. (1913), pp. 727-804, and vol. clxxxix. (1897), pp. 149-166.

† See for instance my book on Electrons, chap. xvi.

diminution of this force due to lateral motion is inevitable. And the resulting lateral expansion or longitudinal contraction, or both, is of the right order of magnitude. So this acts as a previously quite unsuspected compensating effect, which exactly neutralises the drift effect otherwise to be anticipated. Thus, by superposition of two positive consequences of drift, the Michelson experiment, like every other yet made, declines to indicate that there is any drift at all.

Hence, after many such negative results, it seems to become hopeless to enquire experimentally as to our motion through ether. Unless indeed gravitation were exempt from the otherwise universal compensation. In that case the electrical theory of matter applied to the motion of planets might yield a residual result. But my recent enquiry into this problem has suggested that gravitation too is in the conspiracy, and in that case there is some ground for the contention of the extreme Relativists, not only that we do not know our motion—with which everyone agrees—but that we never shall know it: and, in fact, that motion of matter through ether is a phrase without meaning.

I hope we shall not too readily shut the door on further attempts in this direction; and as a conservative physicist I may be allowed to lament the extraordinary complexity introduced into physics and into natural philosophy by the principle of relativity, as so remarkably and powerfully developed by the mathematical genius of Einstein, with complication even of our fundamental ideas of space and time. The complications do not commend themselves to all of us, and I for one should be glad to return to the pristine simplicity of Newtonian dynamics, modified of course by the electrical theory of matter; admitting the Fitzgerald-Lorentz contraction, and admitting also the variation of effective inertia with speed. These things do not destroy, but supplement, Newtonian dynamics. They generalise it in a legitimate and intelligible manner. Such complications as these are clearly in accordance with truth and are to be welcomed; but the complicated theory of gravitation created this century by Einstein, and developed by his successors, and the consequent overhauling of space and time relations, do not at present commend themselves to me, nor I think to others of what I suppose must be called the older school.

Meanwhile the full-blown theory has the courage of its conviction and has predicted a definite result, viz. the deflexion of a ray of light by the sun's limb, equal to 1.75 seconds of arc. The prediction is going to be tested during the solar eclipse of May 29 this year, between Brazil and the Gulf of Guinea. Let the issue be clearly understood. If a star-ray grazing the sun is deflected $\frac{1}{2}$ second it will mean only that light has weight, that the wave-front

* See *The Philosophical Magazine* for August, 1917, and February, 1918, pp. 145, 155 and 166.

not only simulates the properties of matter by carrying momentum—as we know it does from the investigations of Nichols and Hull, Poynting and Barlow, and others—but that it is even subject to gravity. For this would be the angle between the asymptotes of a cometary orbit when the comet is moving with the speed of light and passing close to the sun.* But the principle of relativity—through the refractive or converging influence of a strong divergent gravitational field—demands a greater deflexion than this, more than twice as great. So there are three alternate deflexions before us, to be settled by observation :—

1.75 sec. ; 0.75 sec. ; and zero.

Let us hope that the result of this or of some other eclipse-opportunity may be definite enough to discriminate clearly and quantitatively between these three alternative values ; any one of which should be equally welcome to any lover of truth.

If the first answer is given decisively, it will be a conspicuous triumph for the theory of relativity, and will for a time be hailed as a death-blow to the ether. I claim beforehand that such a contention is illegitimate, that the reality of the ether of space depends on other things, and that the establishment of the principle of relativity leaves it as real as before ; though truly it becomes even less accessible, less amenable to experiment, than we might have hoped. Nevertheless the ether is needed for any clear conception of potential energy, for any explanation of elasticity, for any physical idea of the forces which unite and hold together the discrete particles of matter whether by gravitation or cohesion or electric or magnetic attraction, as well as for any reasonable understanding of what is meant by the velocity of light. Let us try to realise the position beforehand ; for we shall be handicapped in the progress of our knowledge of the relation between matter and ether until these fundamental things are settled, and until everyone agrees that the ether has a real existence. I want people generally to admit that the ether is itself stationary as regards locomotion, and that it is the seat of all potential energy ; and further, at least as a surmise, that it is the medium out of which matter is probably made, and in which matter is perpetually moving by reason of its fundamental property called inertia—a property the full explanation of which must, I expect, ultimately be relegated to and considered as a property derived from the ether itself.

I call this lecture *Ether and Matter*, but I might equally well have called it *Inertia*, for that is the main theme with which I have to deal—at least in this first part.

Is there anything else, besides matter, which possesses or seems

* See, for instance, my paper in the *Philosophical Magazine* for August, 1917, page 93.

to possess inertia? Faraday discovered that an electric current had a property which bore some analogy to inertia, a property clearly depending on its magnetic field. Every current, even a convection current, is necessarily surrounded by lines of magnetic force, and when the magnetic field is intense the current behaves as if it had considerable inertia. Faraday at first called the effect "the extra current." Maxwell called it "self-induction." The latter is the better name.

To show it I start a current in a circuit containing a stout ring of laterally subdivided iron round which the current-conveying wire is wound, and I put in circuit an instrument which only responds when the current has risen to nearly its full strength. A current usually rises, what is called, instantaneously, but here there is a very noticeable delay between pressing down the key and the response of the instrument. [Experiment.] The lag shown is only a second or two, but with care I can adjust it till it is a quarter of a minute. Such delay or lag in establishing a current would be fatal to electric telegraphy. In practice the delay is reduced to a minimum, by using its early values, and the actual response is exceedingly quick. Still, the law of rise of current is quite definite, there is no exception, it is only a question of degree; and the law is the same as that appropriate to the pulling of a barge on a canal. A barge gets up speed slowly, at a rate depending on its mass or inertia, and it ultimately attains a steady speed when the resistance balances the pull.

That is exactly the case of a steady current obeying Ohm's law, the E.M.F. is balanced by the resistance, the propelling force is zero, and the current flows by what we may call its own inertia—its own momentum.

To stop the current you must either increase the resistance or suspend the propelling force. If you interpose an obstacle suddenly, the motion stops with violence—a collision in the case of a train or barge, a flash in the case of electric current. This is what Faraday called "the extra current at break," and if you are holding the wires in your hand when a current is suddenly broken in a circuit of large self-induction you may get a nasty shock.

If you could abolish electric resistance a current would go on for ever without propelling force.

An amazing experiment has been made by Kamerlingh Onnes at Leiden, who first cooled a metal ring down to within four degrees of absolute zero by means of liquid helium, and then started a current through it by a momentary magnetic impulse. Instead of stopping in a minute fraction of a second, as usual, the current went on and on, not for seconds but for days. In four days it had fallen to half strength, and there were traces of it a week later. A most suggestive experiment as to the nature of metallic conduction, as well as a demonstration of the fly-wheel-like momentum of an electric current!

This electromagnetic analogue to mechanical momentum or

inertia is explicable (or supposed to be explicable) in terms of the magnetic field surrounding the current, i.e. really (as I think) in terms of a property of the ether of space. It exactly simulates inertia; but is it an imitation or is it the same thing? Can it be said that an electric charge possesses inertia in its own right, and retains it always, as matter does, whether it be moving or whether it be stationary?

The question was brilliantly answered by your Professor of Natural Philosophy, Sir J. J. Thomson, so long ago as 1881. He calculated the inertia or quasi "mass" of an electric charge e , on a sphere of radius a , and showed that it was $m = \frac{2\mu e^2}{3a}$.

The μ need not be attended to now, though it is really the most important of all—being a great ethereal constant of utterly unknown value*—but for our present purpose the μ merely signifies that the e must be measured in electromagnetic not electrostatic measure, when the formula is interpreted numerically with $\mu = 1$.

At the date 1881 this expression for true electric inertia, though an interesting result, seemed too absurdly small to have any practical significance. Take a sphere like a football, 20 centimetres or 8 inches in diameter; charge it till it is ready to give more than an inch spark, say up to 60,000 volts; then calculate the inertia or equivalent mass corresponding to the charge. If I have done the arithmetic right it comes out one-third of a millionth of a millionth of a milligramme (3×10^{-16}). Absurdly small! Yes, but not zero. And whenever a quantity is not nothing, there is no telling what importance may not have to be attached to it sooner or later. Nothing real can be so small as to be really negligible in the long run as knowledge progresses. Something at present unforeseen may bring it into prominence. So it has turned out in this case. The infinitesimal result of nearly forty years ago to-day dominates the horizon. It was in some sort the dawn of a new era in physics.

Consider it further. Clearly the inertia depends not on the charge only, but on its concentration. The radius of the sphere occurs in the denominator of the expression. The same charge on a sphere 2 centimetres in diameter would have ten times the inertia; on a sphere as small as an atom the inertia would be a hundred million times bigger still. But then even that is small; moreover an atom could scarcely be expected to hold such a charge. Nevertheless, allowing only a reasonable potential, it might seem that atomic inertia could be sensibly increased by an electric charge. But no, even on a sphere as small as an atom the concentration turns out insufficient; the effect is still excessively minute. Yet as electric inertia at given potential depends on linear dimensions,

* I have guessed that it is a density of 10^{12} grammes per c.c. + 4π . See *The Ether of Space*, Appendix 2; also the *Phil. Mag.* for April, 1907.

while material inertia depends on those dimensions cubed, there must be a size when the two are equal, i.e. when one might account for the other.

Write the charge in terms of electrostatic potential V

$$e = K a V$$

then

$$m = \frac{2 K a V^2}{3 c^2}$$

where c is $1/\sqrt{(\mu K)}$, the velocity of light.

Put this expression for m equal to $\frac{4}{3} \pi a^3 \rho$, the ordinary mass.

Then the potential at which the two will be equal is

$$V_1 = a c \sqrt{\left(\frac{2 \pi \rho}{K} \right)}$$

which, for density of water and for a sphere 10^{-13} centimetres radius, is two volts; quite a reasonable electrolytic value, such as is to be expected among atoms.*

The moral of this elementary but not very satisfactory argument is that not for bodies of atomic size, but for something 100,000

* The argument is plausible, and, taken as an illustration on ordinary lines, will serve; but considered seriously it may be quite fallacious, although the main consequences which in the text are going to be drawn are correct. Few things are more surprising than the extraordinarily large charge held by or constituting an electron in proportion to its size. The charge is so large that ordinary arguments about electricity as it exists on material spheres cannot be expected to apply. If they did, or in so far as they do, the potential of an electron would not be two volts but well over a million volts; and the density of the ethereal substance of which it is presumably composed (if its electric inertia is to be derived in any simple ordinary way from its bulk), would have to be nothing like that of water, but of the order 10^{12} , or a billion times the density of water. A thousand tons, in fact, to the cubic millimetre.

We are here out of our depth among quantities on which a great deal of work has to be done to reduce them to order. Yet it must not be supposed that these figures are nonsensical. They require serious consideration; and that is all that can be said for them. I do not think there is any sense in talking about the potential of an indivisible unit of charge, but we can talk about the potential existing at the confines of an atom; and that is a reasonable magnitude, about 14 volts in the case of hydrogen, and not very different for other elements.

But on the other side of the subject everything points to the density of ether being exceedingly high, though perhaps not so high as the above estimate. It must at least be greatly denser than platinum or lead, and probably immensely denser.

A difficulty is often felt as to how ordinary matter like a planet can move through such a medium without friction. Density however does not involve viscosity; the two are disconnected; and resistance to motion would be caused only by viscosity, of which the ether appears to have none. There are many ways, more or less satisfactory, of picturing the perfectly free motion of matter through an exceedingly substantial ether of space; there would be innumerable difficulties in supposing friction and consequent generation of heat. It is quite certain that whatever the ether does it does not dissipate energy. That imperfection belongs to the province of molecularly constituted matter.

times smaller in linear dimensions, is it possible to explain inertia electromagnetically. But, 40 or even 20 years ago, one would have said—there are no bodies of this size; nothing can be smaller than an atom! The strange thing is that, as nearly everyone knows now, bodies of this size have been discovered. They were isolated by J. J. Thomson in 1899, having been gradually led up to by Crookes's and many other experiments on cathode rays; and they are shown to be an apparently invisible unit or atom of electricity whose inertia is wholly electric.

The proof of this last statement I can only briefly indicate. It is established by the effect of speed on electric inertia. If an electric charge is moving with something approaching the velocity of light, its inertia increases without limit; and the formula given about 1889 by Heaviside, Thomson, and others, for electric inertia as a function of speed, is, in its very simplest form,

$$m = \frac{2}{3a} \mu e^2 \left(1 + \frac{v^2}{c^2} + \text{higher powers} \right)$$

The velocity of light squared occurs in the denominator, so, before we can observe the increase, enormous speeds are necessary. A cannon-ball, or even the earth in its orbit, is hopelessly slow; and we know no artificial means of getting up such a speed as this last, viz. about 19 miles a second. But fortunately radium does spontaneously what we cannot do, it expels electrons with something less, but not very much less, than the speed of light; and Kauffmann's measure of the mass of these projectiles, thus flying at prodigious velocities, confirms the theory, and removes any doubt as to the reality of purely and wholly electric inertia, for electrons.

Furthermore it was found that the very same electrons can be split off or detached from any or every kind of atom, that there is only one kind of negative electron; and though at first there appeared to be many kinds of positively charged particles, the evidence is tending to the discovery of a single kind of positive electron likewise; so it is natural to suppose that electrons are an essential ingredient in matter. And since they possess inertia, even those which are clearly disembodied electric charges, it becomes possible to surmise that in some sense, or in a certain grouping, they constitute the atom, that they confer upon it the inertia with which we are familiar and that in fact electric inertia is the only inertia that exists.

Electric inertia began as the simulacrum of material inertia, it has shown itself the very same thing, and it seems likely to end by displacing every other kind of inertia altogether.

This is the electrical theory of matter.

Assuming this theory for the present as a working hypothesis, we may say that material inertia is explained electromagnetically, i.e. is

explained in terms of the magnetic field which necessarily surrounds and accompanies every charge in motion ; since a charge in motion constitutes a current. For on this view a material body is but an aggregate of such charges grouped according to some definite pattern, positive and negative charges interlaced or somehow intertwined, and so far apart in proportion to their size that they do not interfere with each other or cancel each other, nor apparently overlap or encroach on each other's field, to any measurable extent. Is this possible ? It is. For comparing the size of an electron with the size of an atom we perceive that they are relatively of the same order as the size of a planet and the size of a solar system. So it becomes possible to think of an atom as a sort of solar system, with a positive nucleus or sun surrounded by negative electrons revolving in regular orbits round it.

On this view, or indeed in any form of the electrical theory of matter, the atom of matter consists mainly of empty space ; in other words, it is excessively porous ; just as the solar system is mainly empty space and may be spoken of as excessively porous ; the actual material lumps being almost infinitesimal in proportion to the total bulk. A rapid projectile or a ray of light passing through the solar system would be unlikely to hit anything, the chances would be strongly against a collision. So also, if a point be thrown through an atom, the chance of its hitting anything is about 1 in 10,000. It might pass through 10,000 atoms before striking. This experiment has been tried, by C. T. R. Wilson and others, and that is roughly speaking the result. Sooner or later a radium projectile meets with an obstacle and is stopped, but it traverses a good number of atoms on the average ; it traverses quite a perceptible distance even in a dense solid, before it strikes a nucleus.

Matter accordingly seems to me—to us I may say, for in this most physicists are I think agreed—a gossamer or nulky-way structure, an impalpable accident in the substantial ether. Here a speck and there a speck, but, for the great bulk of it, empty space !

“Impalpable” is not the right word, for matter is essentially palpable. It is because it appeals so directly to our senses that we attend to it so vividly. It forces itself on our attention, while the ether eludes us. And why ? Clearly because our bodies are composed—our sense organs are composed—of this very matter. On the material side we are part of, and thoroughly at home in, the material universe. Whereas the ether is elusive ; we know nothing of it directly ; and though our eyes are instruments for receiving ethereal tremors excited by agitated electrons, we only know that fact—or half know it—by rather recondite inference. Light really tells us nothing about its own nature, but only about the superficial aspect of that gross and palpable matter which has interfered with and scattered it before it enters our eye.

Nevertheless the atoms of this solid-seeming flesh and matter as

we know it, when analysed into constituents, are turning out to be composed each of a definite grouping of ultra-minute particles, the positive and negative electrons, which themselves hardly occupy any space (save as soldiers occupy a country), and which appear to be of two kinds only—the ultimate indivisible units of positive and negative electricity.

PART II.—THE POSSIBLE STRUCTURE OF ATOMS, AND THEIR RADIATION.

How then are we to explain the different kinds of matter? Here we enter upon territory so recently annexed as to be still very debatable; but progress has been and is still being made, and it is only through the work of recent explorers that we can attempt to answer the question at all. It is invidious to mention names, but I must mention Rutherford, Soddy, Barkla, Bragg, Moseley, Nicholson, and Bohr, among many others. Moseley—as brilliant as any of them, and patriotically self-sacrificing like all our splendid youth—was killed, alas! by a Turkish bullet at Gallipoli; though not before he had made an immortal discovery. How much more might he not have accomplished had it not seemed good to evil powers to impose by force their dominance on the world!

To give a certain and definite answer to questions about the structure of the atom is premature. I can only state the answer which at present tentatively appeals to me, and I think to others. Your Professor of Natural Philosophy (Sir J. J. Thomson) is lecturing I see on Saturday afternoons concerning spectroscopic evidence on this great subject, and he will no doubt carry the matter further.

Meanwhile, and very briefly, the idea about the atom which at present seems most likely to be on the path towards truth is, a central positive nucleus surrounded by a system of negative electrons—so much is pretty certain—while according to one theory the system is composed of revolving electrons, moving under an inverse-square law in regular orbits, very like the sun and planets. The orbital movement is governed by electric force instead of by gravitation, but the laws of motion, and the perturbations which may be caused by outside forces, are very like those familiar to astronomers.

According to Moseley's experimental counting, and Bohr's theory, hydrogen seems to be like a sun with one planet, just a positive and a negative electron; the two being equal electrically, but differing in inertia, the positive being the more massive, though probably for that reason the smaller or more concentrated of the two. Helium seems to have two central unbalanced positive charges and two revolving negative; lithium, three of each; beryllium, four; boron, five; carbon, six; nitrogen, seven; oxygen, eight; and so on, according to the number of the element in Mendeléeff's series—a number something like half the number expressing its atomic weight.

The number of positive atoms in the nucleus was counted, for several elements, by Rutherford; and the number of negative corpuscles in the orbit was counted by Moseley: the two numbers agree. Normal atoms are therefore electrically neutral, so that their external electric attraction at any reasonable distance is nil; but it is supposed that at atomic or molecular distances the outer or orbital electrons, which can interlock with those of others, determine the atom's chemical affinity and all the chemical behaviour of the substance. An atom with one or two outlying planets—let us surmise—would be an active chemical element, a monad or dyad perhaps. An atom with a close-grouped self-contained system would be an inert element of the argon neon helium series. These might exhibit chemical properties, perhaps, under enormous pressure. The heavier atoms contain the most particles, and must have the most complicated structure. There is every grade; from the simplest, hydrogen, with one electron, to the most complex, uranium, with ninety-two. There is room for ninety-two elements in the series, and no more. All of these are actually known except five or six. There are only these few unfilled gaps in the chemical series of elements as thus planned.

Radioactivity.

A complicated atom has a certain amount of instability and may fall down occasionally into the next simple grouping, flinging away one or more of its units. When this happens there is a sort of atomic cataclysm or explosion, a projectile and some quanta of energy are emitted. This is the phenomenon of radioactivity. Uranium after three (or possibly four) such eruptions becomes the element three (or four) steps down the series, viz. radium. Radium after five more explosions becomes, apparently the well-known and stable element lead, or at least something chemically indistinguishable though perhaps of slightly different atomic weight—what has recently been called an "isotope" of lead. That is the kind of statement that without too much rashness can be cautiously and tentatively made.

At every serious cataclysm an α particle or atom of helium is emitted from the nucleus, accompanied by a β particle or negative corpuscle from somewhere, usually from the planetary system. A sympathetic etherial gush of γ rays accompanies the eruption. A definite unit of energy—a quantum or a simple multiple of it—is emitted at each explosion; and the remaining electrons then settle down into their new orbits, the element changing in character and chemical properties accordingly.

A catastrophe of this kind can be produced by a sufficiently rapid projectile, an α or β particle shot off say by radium; and a minor catastrophe or emission of a β particle can also be produced by the accumulated energy of properly attuned X-rays. When an X-ray or ray of ultra-violet light agrees in frequency with the orbital frequency of an electron, we can suppose (not without a little diffi-

culty) that its energy is absorbed till a quantum has been accumulated, and then a β ray or excessively rapid electron is emitted.

Remarks on the Quantum.

In my view it should not be thought that energy exists in numerical bundles, or quanta; the discontinuity is not really in energy, but in the atom. Atomic properties are essentially numerical and discontinuous, and we ought not to be surprised at an equilibrium which needs a specific amount of energy to upset it. The energy must be supplied by the disturbing impulse; but in the case of ultra-violet or X-ray radiation, the energy can only be attributed to the disturbing impulse on the principle of resonant or syntonistic accumulation; for its intensity does not matter. Nor ought it to matter so long as the tuned impulse is repeated often enough—a repetition for which an extremely minute fraction of a second is ample. What matters is not the brightness or energy of the incident radiation therefore, but its frequency. On the other hand, a β projectile cannot effect a real disturbance unless it possesses a minimum quantum of energy; for in that case there is no accumulation.

The quantum, considered merely as a finite store of energy, is susceptible of exceedingly elementary illustration. Here is a case of stable equilibrium (a simple pendulum, or a round-bottomed flask loaded so as to oscillate stably) which responds to the slightest touch and returns to equilibrium. There is no quantum about that. But here is another case of stable equilibrium (a brick or block or pillar standing on end) which takes no notice of any but a finite force, and which requires a finite amount of energy to upset it—viz. its weight multiplied by the elevation of its centre of gravity as it revolves round its lower edge: this being also the amount of energy emitted when it falls. Or there may be a union of the two kinds of equilibrium. This rounded rocking flask, for instance, or a rocking-horse, may accumulate oscillations till the energy reaches a sort of quantum, when it upsets and breaks or causes an accident. This last is the kind of stable equilibrium which we meet with in an atom.

A flying particle below a certain limit of energy can alter the excentricity of an orbit, and may thus excite some simple radiations which continue till the orbit becomes circular again; but a synchronous X-ray disturbance, however intrinsically feeble, may precipitate a catastrophe; and simple facts of this kind seem to be in the main responsible for the general notion of quanta of energy. The really remarkable thing about a quantum, the thing which makes it so essentially worthy of attention, is the fact that it is a universal constant: the same amount of energy is found associated with every kind of matter—the same, or differing only by simple multiplication. Hence the notion, at one time put forward, that energy itself might be atomic, and exist in indivisible packets, like cartridges.

Hypothetical Structure of Atoms.

The real facts concerning the quantum, which are the result of observation, suggest when interpreted properly that there are stable electronic orbits in an atom, and that these follow a regular law of succession, analogous perhaps to Bode's law of planetary distances in the solar system. Spectroscopic evidence—the so-called Balmer's series of lines—strongly bears out this idea. For there is what is called K radiation, of highest frequency, apparently due to perturbations of the innermost, the most rapid, ring; L radiation of lower frequency from the next outer ring; M radiation from a ring outside this; and recently there is talk of a J radiation of extra high frequency from a ring still closer to the nucleus—perhaps quite close to it, part of it perhaps—and anyway well within the K ring.

The frequencies adapted to bring about an atomic catastrophe, or which are emitted during perturbations, are usually high up in the series of X-ray series of vibrations, far above visible light. I assume that these frequencies correspond with the frequency of orbital revolution, and that the inverse-square law holds good. The more massive the nucleus, the greater must be the frequency of orbital revolution at a given distance, in accordance with Kepler's third law. The square of the frequency multiplied by the cube of the radius of the orbit will be constant for all the orbits of all the atoms of any given substance, and will give the attracting force of the nuclear centre for that substance.

In other words, this product (or, what comes to the same thing, the radius multiplied by the square of the speed) will correspond to the number of unneutralised positive charges which go to make up the nucleus. It will give in fact the number of the element in the Mendeléeff series. The K radiation frequency from uranium therefore must be exceptionally rapid, because the nucleus is so strong. For hydrogen, whose nucleus is only $1/92^{\text{nd}}$ of that of uranium, the orbital frequency might be comparatively slow, not higher than the ultra-violet; while the L radiation from hydrogen, it is now thought, may be within the limits of the visible spectrum; an M series being perhaps in the infra-red.

But how comes it that hydrogen, with only one electron, can have a K series and an L series and an M series at all? Bohr's theory suggests that even a single electron may have alternative orbits—not necessarily occupied; and the spectroscope strongly suggests that the radii of these alternative orbits run as the squares of the natural numbers

1 4 9 16 25 etc.

The frequencies, or reciprocals of periodic times, would then be as the inverse cube of the natural numbers

1 $\frac{1}{8}$ $\frac{1}{27}$ $\frac{1}{64}$ etc.,

and this is approximately and roughly what the K L M series of spectrum lines correspond to—with some exceptions.

When a cataclysm occurs and an electron is expelled, it is expelled as I think with the velocity which it possessed in the atom just before it burst its bonds and flew off. For the energy required to fling a planet to infinity, under an inverse-square law, is just double the energy with which it was already moving in its circular orbit. Its own orbital energy is therefore the quantum of energy that has to be supplied in order to get a satisfactory ejection. Some of it might be supplied by the falling in of other particles from their original orbits: for their kinetic energy therein would be inversely as the distance from the nucleus. Hence if K, L, M orbits have the radii 1, 4, 9, three units of L energy would represent the fall from L to K, and this added to the original L energy would give the quadruple L energy which is equal to the K energy, and able to eject a K particle. Similarly a ninefold multiple of the M energy, eight units of which would be acquired by falling to K, would supply that particle with the ejection energy, equally well.

Would an M particle falling to L be able to eject an L particle? $\frac{1}{4} - \frac{1}{9} = \frac{5}{36}$: if a K unit of energy would be acquired in the fall from M to L, that is $\frac{2}{9}$ M units, so altogether $\frac{5}{36}$ of M energy would be transmitted, and that, being equal to a unit of L energy, ought to be sufficient.

Hence, in general, particles may be ejected from any ring, either by direct impact from outside, or by accumulated disturbance of X-rays, or by a collapse of particles from one orbit to the next; and from an immense group of atoms, as in a visible speck of substance, all kinds of radiation can be emitted simultaneously.

Are we to suppose that there is only one electron in each orbit, or may several of them distribute themselves over a ring in accordance with some law of stability? Both alternatives are possible, and both are likely to be found in nature. It seems hardly likely that a uranium atom should possess 92 different orbits, although it does contain 92 electrons. Yet even this number of orbits is possible within the dimensions of an atom. We need not exclude the possibility, as taking up too much room. For given the size of the ultra-innermost or J orbit as 1, the outer orbit would, on Bohr's law pressed to extremes, be $(92)^2$ times that radius, say 8464 times the size of the innermost orbit; but if this innermost orbit is near the uranium nucleus, which may be $\frac{2}{3}92$, or say 5 times the radius of the hydrogen nucleus, the boundary or confine of the atom is some 10,000 times as far away; leaving therefore just room enough for the 92 Bohr orbits, though not much more than is required.

Hence if there were any reason to desire them separate, they could be made room for, without endowing the atom with outlying or ever-ready electrons likely to confer upon it very active chemical properties. But so far as I see, so many separate orbits are not

likely ; for there is every probability that periodically, as you ascend the series, the outer ring is not occupied by a single electron but by a closed compact sort of structure of many electrons, with very little outside affinity, so that we reach periodically an atom which is chemically inactive, helium, neon, argon, krypton, etc., up to emanation, or what Ramsay called niton. So little cohesion holds between such atoms that they are able to exist as permanent gases in spite of the high density of some of them. This at least appears to be the view of Rutherford and Soddy. Helium only condenses to a liquid when cooled down to near the absolute zero of temperature. Its cohesion or intermolecular attraction is nearly nil.

A Fanciful Analogy.

If I attempt to compare the supposed alternative orbits in an atom with the known orbits of the solar system, it is mainly to emphasise, provisionally and tentatively, and perhaps semi-humorously, the astronomical view of the atom ; and to bring out still more strongly the resemblances, whatever thorough differences there may be as well.

I write down the squares of the natural numbers, therefore, and underneath put the names of planets, with its real distance written under each in the same units.

Radii of Bohr's atomic orbits	1	4		9	16	25	36	49	64	81	100	121	144	169	196
		m		E	M	Asteroids		J			S				U
				V											
Planetary distances	}	3.9	7.2	10	15.2	20-35	52				95.4				192

The obvious suggestion is that asteroids should be looked for between Jupiter and Saturn, and between Saturn and Uranus ; but I would not venture to predict the existence of any such bodies on the strength of this analogy, because you will doubtless have noticed that no analogue of the planet Venus appears in the list of atomic orbits ; the scheme provides no place for her—a lamentable omission which must discredit and I expect condemn even the analogy. Nevertheless I make no apology for introducing it, in order to emphasise astronomical similarities in the possible structure of an atom.

QUANTITATIVE INTERPOLATION.

On Atomic Radiation.

Permitting ourselves this view of the atom as a working hypothesis, we have to picture each atom as an attracting centre or nucleus, with a number of alternative orbits in regular succession round it, but not all necessarily occupied by revolving electrons.

The atoms of different elements differ in the number of positive units in the nucleus, and in the corresponding number of revolving negative units; in fact the diverse chemical elements, in their atomic constitution, form a definite arithmetical series with common difference one. There is a discontinuity or finite step in passing from one element to the next in the series, there is no continuous passage from one to another; hence if the physical transition or mutation ever occurs, it must be by some sort of sudden convulsion.

To extract laws for this hypothetical structure, suggested by the labours of many workers, we may attend to the different rings of one kind of atom, or we may attend to the corresponding rings in different kinds of atom. Each, for instance, has an innermost ring, which it is convenient at present to call the K ring, because of the shortest wave lengths, or so-called K spectrum, which its perturbations emit. And, in ascending the series of elements, as the nucleus gets stronger by addition of units, the electron in this innermost or K ring must revolve faster and faster to counterbalance the greater attracting force. Its orbit will accordingly get smaller and smaller, in the proportion proper to the law of inverse square. And the frequency will increase for both reasons, i.e. for both the greater speed and the shorter journey. The spectrum accordingly, while preserving the same type, ascends the ladder of frequency.

Suppose the atomic number, or strength of the nucleus in atoms of successive elements, increases in arithmetical progression $N - 1$, N , $N + 1$, etc., then the radius of the given type of orbit may shrink in the same proportion, so that rN is constant; and the velocity v may increase in the same proportion, so that rv is constant; or in other words so that the moment of momentum in corresponding rings of different atoms is the same. There is good evidence that such is the case. The law, so far as it is a law, is styled by Professor Millikan, the atomicity of angular momentum. If the value of $mv r$ or $mr^2\omega$ differs in different rings, it differs by finite steps.

The frequency of orbital revolution will depend on v directly and on r inversely, so the frequency ($v/2\pi r$) will increase in the proportion of N^2 ; and this, in some form or other, is known as Moseley's law.

The energy, $\frac{1}{2}mv^2$ in a given type of ring, will also depend upon N^2 in different atoms, and is therefore simply proportional to the frequency. The orbital energy is half the energy with which a particle breaks loose (or is driven to infinity) whenever a convulsion occurs. The convulsion can be stimulated by X-rays or ultra-violet light of the right frequency; their energy appears to be stored by resonance until the critical breaking-up point is reached. The ratio of emission energy to frequency is a remarkable universal constant, and is called h , the quantum. It is not energy, but the accumulation or integral of energy for a certain time; and it is permissible to

write $m v^2 = 2 m u^2 = h n$; because the emission velocity u (the velocity from infinity) is $\sqrt{2}$ times the orbital velocity v . But h , or rather $h/2\pi$, may also be taken as representing the orbital angular momentum, $m v r$ (more strictly, if the orbit is at all elliptical, $m v p$) for the ring whence the particle came. It would be rather convenient if the designation h were transferred to $h/2\pi$ before it is too late; but I must leave this minor change to the approval of leaders in this subject.

I may point out that this constancy of angular momentum in different orbits bears a curious analogy to Kepler's second law about rate of description of areas in the same orbit. And, if a coincidence, it is odd that the symbol h should have been used both for Kepler's $r^2 d\theta/dt$ and for an atomic quantity which is also $r^2 d\theta/dt$ multiplied by $2\pi m$.

Within each atom Kepler's laws must presumably hold; so r^3/t^2 , or $r v^2$, is constant for the different circular orbits in each atom; whence the energy in successive rings of one atom is inversely as their radii; hence the ring most likely to eject a particle is the innermost or K ring.

This characteristic constant $r v^2$ of an element is proportional to the central attracting force, and therefore proportional to N . Hence it goes up step by step in the series of atoms, as N does.

Summary.

N is Moseley's atomic number, and equals the number of orbital electrons, or the number of unbalanced positive charges in the nucleus. The constant $r v^2$ is characteristic of all the rings in one atom (N being constant). The product $r v$ is a constant characteristic of a given type of ring in the whole series of atoms (N going up step by step); but in any one atom this product $r v$ ascends from ring to ring in regular arithmetical stages, the same stages as \sqrt{r} .

The product $r v^2$ is constant inside each atom and proceeds by steps from atom to atom; while the product $r v$ is the same for different atoms, but changes inside each atom and proceeds by steps from ring to ring. In fact we may write:—

For all the rings in one atom.

Central force	$r v^2$ is constant.
Angular Momentum for the rings in one atom	
Energy for the same	
					$r v \propto \sqrt{r}$
					$v^2 \propto 1/r$

For any ring in any atom.

Central force for any ring in any atom	$r v^2 \propto N$
--	-------------------

For the same type of ring in different atoms.

Radius of given type of ring in any atom	r	\propto	$1/N$
Orbital Velocity in ring of that type	v	\propto	N
Moment of Momentum in given type of ring	$r v$ is const. as regards N .		
Frequency in that type of ring	v/r	\propto	N^2
Energy in same	v^2	\propto	N^2

So for a given type of ring in different atoms the orbital energy is proportional to the frequency ; which is a curious result thoroughly consistent with Moseley's law, ascertained by experiments on emission, and true at any rate for emission energy.

The ratio

$$\frac{\text{emission energy}}{\text{frequency}} = \frac{m v^2}{v/2 \pi r} = 2 \pi m v r = 2 \pi \cdot m r^2 \cdot 2 \pi r = 2 \pi I \omega$$

So if we call this h , or a multiple of h , then on our hypothesis $h/2 \pi$ is the indivisible unit of angular momentum for an orbital electron.

The speed with which an electron is ejected is very high, something like 0.9 of light, so the increase of mass at high speeds must be taken into account in propounding a reason for the emission of corpuscles.

Radiation Heterodoxy.

In considering the radiation from an atom I have virtually made the hypothesis that so long as orbits are circular they do not radiate, but that if perturbed into ellipses, with corresponding fluctuation of speed—as they would be by the influence of a flying charge passing through or near them—then they would radiate, with the proper orbital frequency, until the excentricity disappears again and they resume their stable circular orbit once more. Though of course they might be so much perturbed as to eject a particle. Any one of the rings, if perturbed at all, may radiate and give appropriate spectral lines. An external synchronous alternating field will also cause them to absorb energy, even though they were not radiating any until the extra energy arrived.

This hypothesis, if at all regarded, is equivalent to a request to mathematicians to reconsider their theory of electronic radiation. Radiation intensity is known to be proportional to the square of acceleration (Sir Joseph Larmor, and to some extent FitzGerald and Hertz, established this), and I must admit that the reasoning seems to make this law applicable to every kind of acceleration ; but my rash suggestion is that it may be only speed-acceleration that is really effective, and not transverse or curvature-acceleration at constant speed. For this will not perturb the lines of force holding the electron to the nucleus. but will leave them in a constant condition,

so long as the orbit is circular and the speed therefore constant. There is a recognised difference of the same sort in connection with varying inertia; its value is not affected by transverse acceleration, with the speed left constant, but it is affected by longitudinal acceleration, which alters the speed.

So I am in hopes that it may be found that this latter or speed-acceleration is what is responsible for radiation, and that mere curvature at constant speed in a circular orbit need not radiate at all. Provided always that the superposition of an external alternating field of the right frequency may cause absorption. Many of the difficulties connected with the stability of the astronomical atom would be evaded if the theory of radiation could be modified in this way; and the excitation of characteristic radiation by almost any kind of perturbation of the orbit would be intelligible.

Speculations on Radiation and Atomic Structure.

Bohr's remarkable theory of atomic structure does not pretend to be strictly dynamical; it is partly empirical, being based on the discontinuity signalled by Planck's constant, but it is very brilliant, and extensively justifies itself by agreement with facts.

His expression for the frequency of radiation emitted by any element is virtually, to a fair approximation—

$$n = \frac{2\pi^2 me^4}{K^2 h^3} \cdot \left(\frac{E}{e}\right)^2 \left(\frac{1}{p^2} - \frac{1}{q^2}\right)$$

where $\frac{E}{e}$ is Moseley's atomic number, N the number of unbalanced charges in the nucleus or the number of electrons in the atom, and where p and q are integers of which p changes from series to series, while the lines in each series are given by the mutations of q . For heavy atoms the E in the above formula should be E minus a geometrical function of all the other electrons inside the radiating orbit, because they will affect the central attracting force. In this way outstanding discrepancies may plausibly be explained. But the remarkable thing is that the formula gives the frequencies not merely relatively but absolutely. For if the experimental values otherwise obtained for e , m and h are inserted, the constant outside the brackets, called Rydberg's constant, which is spectroscopically determined and known to be the same for all elements, comes out right. A very notable fact!

The above expression for spectral lines not only agrees with the Rydberg-Balmer known spectroscopic series, and with the kind of formula given by many pioneer workers, but has been able to predict other series which have been subsequently observed. It also accounts for many extra-low-frequency lines which though not obtainable in the laboratory are observable astronomically, by suggesting that

they come from very large masses of highly rarefied gas. For under such conditions the atoms would have more room and could possess far outlying or ultra-Neptunian electrons, and yet have total substance enough to display their spectra.

To contemplate the emission of radiation, both waves and particles, we may picture one of the satellite electrons in a many-orbited atom struck or so thoroughly perturbed by the sudden arrival of a foreign charge as to precipitate it into the next inner ring, ejecting the constituent of that ring into the one below, and so on, after the manner of the "jack for mustard" game with a series of wooden bricks set up on end.

Wave emission should accompany each transition. The effect of precipitating the innermost electron on the body of the nucleus is not clear; but a compound nucleus must be a strangely interlocked conglomerate, and an explosion seems not unlikely: especially if one of the supposed binding negative electrons were ejected. The potential gradient close to a nucleus is prodigious.

The effect of the arrival or departure of a charged particle at the nucleus would be suddenly to change its intrinsic attracting force; and this of itself would render all the orbits elliptical for a time, with excentricity $\frac{1}{N \pm 1}$,* thus exciting radiation of several frequencies. If the radiation ceased when the excentricity was got rid of, a new circular orbit would be taken up, and thus perhaps discontinuities might be accounted for in a dynamical manner.

The effect of properly attuned X-rays or ultra-violet light, if it is to be accomplished through resonance—and it is difficult to account for its

* This can be proved as follows.—

For a circular orbit

$$r v^2 = \mu$$

and

$$r^2 v^2 = h^2 = \mu r.$$

When μ suddenly changes to $k\mu$ (where k may be $\frac{N \pm 1}{N}$) the velocity does not instantly change, but the orbit acquires an a and an e , such that

$$a(1 - e^2) = \frac{h^2}{k\mu} \text{ or } e^2 = 1 - \frac{r}{k a};$$

also

$$\frac{\mu}{r} = v^2 = k\mu \left(2 - \frac{1}{a} \right).$$

This last gives

$$\frac{r}{a} = 2 - \frac{1}{k},$$

$$\begin{aligned} e^2 &= 1 - \frac{1}{k} \left(2 - \frac{1}{k} \right) \\ &= \left(1 - \frac{1}{k} \right)^2. \end{aligned}$$

And the place where the sudden impulse occurred becomes an apse of the new orbit, because $r = a(1 \pm e)$. (See also Appendix I.)

independence of intensity otherwise—seems to require a fair range of frequency in those rays; for their effect on a revolving electron would naturally be to increase its angular speed and so throw it out of tune with the particular disturbance to which it initially responded. The sectorial area swept out would increase, the radius vector would increase, the linear speed would therefore diminish in spite of the resonant effort to increase it. Unless indeed, under the peculiar conditions in an atom, there may be some compromise. The alternative would be for the electron to be constrained, under conditions of stability, to maintain its frequency unaltered, either proceeding in an outward spiral towards a position of Planckian instability, or trying still to obey the law of inverse squares by increasing the ex-centricity of its orbit with given axis major until it becomes practically parabolic. (*See Appendix II.*)

This could represent an inversion of the process by which the electron may have been originally bound, according to Bohr's theory of what happened before the atom became neutral. For it is to be presumed that a positively charged α particle, after ejection, neutralises itself by accretion and settles down.

CONCLUSION.

I have led you over a great deal of territory in a hurried manner, and occasionally have entered on regions where the ground is not yet solid and secure. Let it be granted that the chemist may naturally object to an astronomical atom and may prefer a more static or geometrical structure, although such a structure would have less clear and explicable properties. The static or Boscovich atom, with purely hypothetical interior fluctuations of force, leaves everything in the dark, and is therefore less tempting to a physicist, until some physical explanation of those fluctuations can be given. At present they seem to be postulated merely in order to secure positions of equilibrium in which an electron can settle down. Orbital revolution achieves the same end, in apparently a more complicated but really a more tractable manner. Moreover it confers upon an atom the sort of energy and structural velocities which are conspicuous in the various types of radio-activity. True, it is a working hypothesis at present, and nothing more, but it seems likely to be a fruitful one; and that is its present justification.

The subject is in the nascent or rapidly growing stage; and, provided we refrain from dogmatism, it is legitimate thus tentatively to survey and explore the boundary between knowledge and ignorance, and to speculate as to what may be the next stages in the exhilarating pursuit.

The apparent resemblance between an atom and the solar system opens up extraordinary vistas for further enquiry. Optics and

gravitation still have many secrets. The interactions between ether and matter are as yet barely understood. We know that the energy of an electric current is really in the ether, i.e. in the magnetic field surrounding the current; but we must admit that the electromagnetic explanation of inertia is no ultimate explanation—it is but relegating the property to some fundamental property of the ether; of which substance presumably matter itself may in some way be composed.

Evidence suggests that the ether is an excessively dense substance, and that it circulates slowly along lines of magnetic force.* But though so dense we have no means of apprehending it directly. Matter, though so comparatively filmy and fragmentary, yet looms large in our estimation because of our material sense organs; its properties force themselves on our attention because in fact our bodies are composed of matter. But underneath and behind all the known properties of matter lie the unknown properties of the ether of space; and if we are to create a true philosophy we must attend continually to Ether as well as to Matter in the physical universe. The ether makes no appeal to our senses, but it is none the less real for that. Sensation is no test of reality: many of the most important things are in the insensible universe; and he is the wisest man who shuts the door on no opportunity for investigation, but keeps his mind open, and is ready to explore every avenue towards truth.

[O. J. L.]

APPENDIX I.

EFFECT ON ELECTRONIC ORBITS OF SUDDEN NUCLEAR CHANGES.

Continuing the subject of the footnote on page 473, and taking the case of an atom degrading by radioactivity, though an inverse process of ascension by building up light atoms into heavy ones can be equally dealt with if that process ever now occurs; let us assume that a nucleus expels first a negative unit and then a positive unit. At the first emission the nucleus, with N unbalanced positive charges, suddenly gains force in the ratio $k = \frac{N+1}{N}$.

The result on its family of revolving electrons is to make every circular orbit elliptical. With the usual Tait and Steele notation, initially $R V^2 = \mu$. When the change occurs the semi-major axis of the new orbit is given by

$$\frac{1}{a} = \frac{2}{R} - \frac{V^2}{k\mu} = \frac{1}{R} \left(2 - \frac{1}{k} \right);$$

hence

$$a = \frac{N+1}{N+2} R, \text{ and } e = \frac{1}{N+1}.$$

* This view of the energy of a magnetic field, that it is direct kinetic energy of the ether moving longitudinally, suggests a possible (or nearly impossible) experimental means of determining the real density of the ether of space—a subject on which I have much more to say. See probably *Phil. Mag.* for May, 1919.

The next disturbance—the emission of an α ray and another β ray—may be expected to occur, by preference, when the quasi-tidal power of the electron is greatest, i.e. when it is at the nearest apse, or when several of the innermost particles are in conjunction there. Granting this for the moment, the velocity of any one of them at that place will be

$$V'^2 = k\mu \left(\frac{2}{R'} - \frac{1}{a} \right) = \frac{k\mu}{a} \cdot \frac{1+e}{1-e}.$$

With this speed, or something near it, the particle is projected into its final orbit, the central force being now restored to its old value, though the atomic weight has gone down a step. The semi axis major of the final orbit is independent of the direction of projection, and is given by

$$\frac{1}{a'} = \frac{2}{R'} - \frac{V'^2}{\mu},$$

whence

$$a' = \frac{a(1-e)}{2-k(1+e)} = \frac{N^2 a}{(N+1)(N-2)} = \frac{N^2}{N^2-4} R.$$

The frequency is inversely as the $3/2$ power of a' , the excentricity is $e' = \frac{2}{N}$, and the new radius differs from the old one by the ratio

$$\frac{N^2}{N^2-4};$$

an expression which looks as if it ought to account for Balmer's series of spectrum lines.

APPENDIX II.

EFFECT OF SYNCHRONOUS ULTRA-VIOLET OR X-RADIATION.

Referring to pages 465, 470 and 474, about storing a feeble disturbance by resonance, the equations of planetary motion are

$$\ddot{x} = -\mu x/r^3 \text{ and } \ddot{y} = -\mu y/r^3.$$

Upon this we have to superpose a train of waves of very small amplitude

$$y = \kappa \cos \frac{2\pi}{v\lambda} (x - nt),$$

where n is to be the "mean motion" of the planet, $n = \sqrt{\left(\frac{\mu}{a^3}\right)}$.

The essential part of this can be presented as $\dot{y} = -n^2 y$ to be added the main term. Hence the equations become

$$\ddot{x} = -\frac{\mu x}{r^3}; \quad \ddot{y} = -\mu y \left(\frac{1}{r^3} + \frac{1}{a^3} \right), \text{ and } r^3 \frac{d\theta}{dt} \text{ is the integral of } -\frac{\mu xy}{a^3}.$$

On submitting these equations to Mr. C. T. Preece, Mathematical Lecturer at Birmingham University, he dealt with them thus:—

$$\dot{x}^2 + \dot{y}^2 = \frac{2\mu}{r} - \frac{\mu}{a^3} y^2 + U,$$

or choosing the constant suitably—

$$v^2 = \mu \left(\frac{2}{r} - \frac{1}{a} \right) + \frac{\mu}{a^3} (\kappa^2 - y^2).$$

The second term represents departure from elliptic motion by the planting on it of a small harmonic disturbance.

If the disturbance ceases at any point (x, y) the particle will continue in an ellipse, such that—

$$a' = \frac{a^3}{a^2 - \kappa^2 + y^2}.$$

The effect of the disturbance, while it lasts, is to shut up the ellipse spirally in the direction of its minor axis, leaving the major axis considerable, the eccentricity of the orbit becoming great. In the limit the semi-minor axis might be reduced to κ , in which case $e = \sqrt{1 - \left(\frac{\kappa}{a}\right)^2}$, and the possible range of a' would be between a and a/e^2 . So practically e becomes nearly 1 and a' remains nearly a ; thus keeping the frequency constant.

The effect of this narrowing down of the ellipse is to bring the particle within the range $\kappa \sqrt{\frac{1-e}{1+e}}$ of the central nucleus, or practically $\frac{1}{2} \frac{\kappa}{a}$ —a proximity likely to cause disruption and conferring on the particle a high maximum velocity $na \sqrt{\frac{1+e}{1-e}}$, or approximately $\frac{2}{\kappa} na'$.

This looks as if we could thus reckon an exaggerated upper limit to the amplitude of light-wave concerned. With ordinary electric values for m it comes out $\kappa = \sqrt{(6 N a z)}$, where z is the size of an electron, and a the size of its orbit; but if m is allowed to increase with speed, β being the ratio v/c , this expression for the minor axis of a disruptive orbit, $\sqrt{(6 N a z)}$, must be multiplied by the fraction $1/(1 - \beta^2)/\beta$. It seems anyhow to be of the order 10^{-10} centimetre.

Friday, May 2, 1919.

GENERAL E. H. HILLS, C.M.G. D.Sc. F.R.S.,
Secretary and Vice-President, in the Chair.

PROFESSOR JOHN W. NICHOLSON, M.A. D.Sc. F.R.S.

Energy Distribution in Spectra.

OUR knowledge of the structure of very fine spectrum lines is now on a secure and nearly comprehensive basis, from the point of view both of theory and of experiment, and it is very remarkable that so little is known of the distribution of energy in these lines, either in individual lines, or as between the different lines contained in the spectrum of any atom. The analysis of the spectra of atoms, theoretically and in the laboratory, is now recognised as the most critical test to which any theory of atomic structure can be subjected, and we have recently had theories of the atom entirely based upon the wave-lengths of the radiations which they emit. A question of equal importance, to which I now wish to direct your attention, is the relative amounts of energy which the atom throws out in the different wave-lengths, for this is well known to vary in some cases very greatly, according to the circumstances under which the atom is excited. I shall describe, in the first instance, a method designed by Dr. Merton for investigating the distribution of energy among spectrum lines, or in the breadth of an individual line, with great accuracy. It is possible by this means to obtain the long-desired object of an absolute scale of spectral intensity, independent of all the ordinary difficulties determined by such matters as the unequal behaviour of the photographic plate for light in different regions of the spectrum. Dr. Merton and I have been working together on this subject for the past three years, and I shall conclude the present discourse with an account of some of the more interesting results which have been reached, after an explanation of the method.

The intensities of spectrum lines have usually been recorded on an arbitrary scale, ranging between 10 and zero, the numbers assigned being at the discretion of the observer, and varying so greatly among different observers as frequently to be of little value for exact knowledge. They depend also very much on the nature of the observation, whether visual or photographic, and in the latter case, on the region of the spectrum to which the line belongs. The sensitivity of a photographic plate varies with the wave-length of

the light in a curious manner, and apparently an irregular one not following any simple law. The sensitivity of the eye is also different for different colours.

When the line is outside the visible spectrum, in the infra-red or dark heat region, measurements of intensity can be made with some accuracy by a thermopile or a bolometer. But they are needed more urgently in the visible region at present, not only for the information they will afford regarding the nature of the atom, but also for application to other problems. The subject is very important, for instance, in the interpretation of celestial spectra, and more particularly those spectra of great complexity and variability which are associated with the birth of new stars, from which most of our knowledge regarding such stars must be constructed.

Previous knowledge of changes in spectral intensity under varying conditions was of necessity limited to the great changes. Those changes which are of especial value in connections such as I have mentioned are liable to be of a less conspicuous type, not readily capable of detection by the ordinary photographic or the visual method, and if detected, not capable of accurate measurement.

In the visual region of the spectrum, observations with the bolometer are not satisfactory. The source of light must be very intense in order to produce large deflections in the galvanometer, and only the brightest lines could be dealt with even in this way. Only one line in the spectrum can be experimented upon at a time, and the source of light cannot be maintained constant over a protracted period. The method is in fact quite unsuitable, and the spectrophotometer has been tried instead, but no great accuracy is possible, and its use is confined to a very narrow region of wave-length. Moreover, the variability of the source of light is again present.

In adopting any photographic method for quantitative work, we must remember that not only does the sensitivity of the plate vary with the wave-length, but also that there is no very definite relation between the density of a photographic image and either the intensity of the light or the time of exposure. If we halve the former and double the latter, we do not get the same density of the image, but another which depends on the particular plate used. The grain of a plate also scatters light, and the critical size of the image thus depends on the exposure and the intensity of the light. We were early compelled to conclude that accurate measurements of intensity by a photographic method involve the necessity of an equal exposure on the same plate for all the sources of light to be compared, and the method to be described satisfies this necessity.

The spectrograph for producing and photographing the lines of a spectrum is set up in the usual way, which requires no description. A wedge of neutral-tinted glass, cemented to another of clear glass so as to form a plane-parallel plate, is mounted in front of the slit. The image of the slit formed by light of any wave-length is thus

attenuated towards the part of the slit opposite the thick end of the wedge, where the absorption of light is greatest, and the image ceases to be strong enough to affect the plate beyond a certain specific height which depends on the original intensity, in the beam from the source, of this particular wave-length.

The photograph thus consists, not of the usual spectrum with all lines or slit-images of the same length, but of a spectrum in which all the lines are cut down to specific heights depending on the original intensities, and thus it gives a simultaneous record of all the intensities in the spectrum at any one instant. All spectrum lines have a breadth, due to Doppler effect of the atomic motions in the kinetic theory, and to other agencies. The shape of one of the truncated lines depends on the original law of intensity across the line. This shape may be a wedge, or may be bounded by a more or less rounded curve, from whose nature, if the boundary can be defined sharply, we can deduce mathematically the law of intensity across the original line. Sharp changes of intensity, such as occur when the line has several close components overlapping one another, are detected as peaks or kinks in this bounding curve. The original photograph can be enlarged with considerable magnifying power, and if the bounding curve on this enlargement is sharply defined, we can obtain its mathematical shape very accurately, and deduce an estimate of the intensity in any part of the line with a great degree of precision. We have been able to show, for instance, that in most of our experiments, such accuracy as one part in 100 has been reached, and it could be increased readily if desired by the use of greater magnification of the original photograph.

The determination of the exact boundary of a patch of dark on a white ground is a matter in which "personal equation" is important. We overcame this difficulty by enlarging positives, prepared from the negatives, on to bromide paper through a ruled "process" screen. The resulting photograph consists in this way of an assemblage of very minute dots, fading away towards the boundary into invisibility. It is a simple matter to prick out the last dots visible all round the contour, and in this way personal equation can apparently be entirely eliminated. We adopted usually about 100 dots to the inch on the final photograph. If comparisons of different lines with the another are required, only the central heights of the figures are necessary, and the topmost dot can be seen at once.

The first application of the method was to the intensity distribution in the lines of the hydrogen spectrum when a condensed discharge was passed through the exciting tube. It was known that with a condensed discharge the lines always appeared much broader, and we concluded that the best method of obtaining information as to the source of the effect was to examine the intensity distribution across the lines. Some remarkable contours were obtained, showing at once a clear distinction between this source of broadening and that

associated with the Doppler effect. The contours associated with the latter should be thin symmetrical parabolas. Those we found were wedge-shaped, with definite kinks indicating the introduction of new component lines when the condenser was put into the circuit. The wedge-shape indicates that the law of decrease of intensity from the centre of a component is exponential, and not the law of error as in the Doppler effect. By measuring the distances between the kinks, and knowing the magnification and a previous calibration of the wedge, all necessary quantitative data of the spectrum line can be calculated. It was possible to show, in particular, that the separations in wave-length of the components of H_{α} were those found by Stark when new components were called into being by the existence of an enormous external potential gradient. As we had suspected, the origin of this exceptional broadening under the condensed discharge is the "electric Zeeman effect," the origin of the large electric field on any atom being the close proximity of other charged atoms. We thus have a new means of studying the electrical resolution of spectrum lines, more convenient in many ways than the older methods, and capable of much greater generality and accuracy. A large number of observations of the same phenomenon were made also on the spectrum lines of helium and lithium, and the correspondence with the Stark effect always held good.

The examination of an individual line has also been applied in the case of an "ordinary" discharge, and given the first direct proof of the probability distribution of velocities in the radiating atoms of a gas. This distribution has been taken as a basis by Lord Rayleigh in the elaboration of a precise method of determining the mass of a radiating atom from the breadths of the spectrum lines, a method applied by Buisson and Fabry with great success, when the breadth is measured by methods of interference of light. Our experiments have defined very closely the circumstances in which this method is practicable, and shown that it fails altogether if condensed discharges are employed. In the ordinary uncondensed discharge under low pressure, however, our contours are very accurately parabolic, which fact can be shown to imply a very rigorous probability law of velocities in the atoms, and no other important source of broadening of lines in these circumstances.

The only other application to an individual line which I shall mention concerns the nature of the Balmer series of hydrogen, long believed to be a Diffuse Series, with each line consisting of two close components, hardly separable or not separable at all, with the same interval in frequency between them for every line. We have shown that it is in fact a Principal Series, with the separations decreasing in a calculable way required by theory, conforming also the separation in H_{α} given by Buisson and Fabry. The method was to use the neutral wedge in combination with another apparatus of extreme resolving power—in this case a Lummer-Gehrcke plate. We can in

this way obtain contours for a pair of close components which cannot be detected visually as a pair, and the actual interval can be deduced by a series of measurements of the joint contour, consisting of two overlapping parabolas. We calculate the position of the vertex of the inner one, and thence the separation, which can, in H_{β} , be determined within about 0.001 of an Ångström unit. The actual separation in this line is as small as 0.030 Å., and the present method could measure accurately a much smaller separation.

We pass now from the phenomena of structure and intensity of a single line to those involving a comparison of different lines. Here the behaviour of the plate for different wave-lengths must be dealt with. But it so happens that every plate can be calibrated by throwing on to it not only the whole spectrum under examination, but the radiation—a continuous spectrum—from the positive crater of the carbon arc. The energy distribution in this case is known from Wien's law when the temperature of the arc is known, as it is very closely. On the slide you will notice the curious contour bounding this spectrum, largely due to vagaries in the sensitivity of the plate. Above it is the helium spectrum on the same plate. To obtain an absolute scale of intensities down the helium spectrum, independent of all sources of error due to apparatus, we only need to compare the heights of the lines with the corresponding heights directly below them in the carbon-arc spectrum. It is in fact logarithms of intensity which the heights represent, and the differences of height represent powers of a definite *factor* entering into the intensities, so that the photographs give no visual impression of the enormous differences of intensity which occur. For example, the line of wave-length λ 3888, a Principal line in the helium spectrum, appears quite short on the photograph, but is actually the most intense in the spectrum. Absorption in the apparatus is strong in this region. One of our conclusions, in fact, is that Principal Series deserve their name even in elements which appeared hitherto to be exceptions, in that they do contain, for the visible region, a preponderant part of the radiated energy.

It is not necessary to use the carbon arc in every subsequent experiment. We can by its means calibrate the helium spectrum under conditions easily reproduced, and subsequently take this as our standard, especially when the work projected is the variation of the helium spectrum under changing conditions of excitation. Some of the remaining slides indicate the unexpected character of some of these variations. It would not be possible in this Discourse to give anything like a complete account of the phenomena of this class already investigated, and I shall therefore confine myself to some of those which are most striking. In the first place we may notice the spectrum of a mixture of hydrogen and helium or neon. The fundamental phenomenon which this method has detected is what we have

called "transfer of energy along a series." For instance, in the Balmer series of hydrogen, produced from pure hydrogen under "ordinary" conditions, there is a perfectly definite intensity relation among the lines H_α , H_β , and so on; but in the presence of helium this is disturbed, and the ratios H_β/H_α , H_γ/H_β , H_δ/H_γ , . . . are notably increased. In other words, more energy tends to be emitted in the form of the more refrangible rays, at the expense of the less refrangible. It is interesting to speculate as to how far this process can be carried, for its logical outcome is a radiation from hydrogen concentrated at $\lambda 3646$, the limit of the Balmer series. We have not in fact examined the matter from this point of view.

Neon produces the same effect on the hydrogen spectrum, the first recorded evidence being an experiment of Liveing and Dewar, who found in 1900 that it was possible to observe more of the violet members of the Balmer series when neon was present. We have made quantitative measurements of the effect in various cases, and in one experiment, for instance, the neon was found to make H_β $\frac{6}{5}$

as strong, H_γ $\frac{9}{5}$ as strong, and H_δ $\frac{11}{5}$ as strong, in relation to H_α .

But I shall not enter into further numerical detail. A particularly interesting fact is that the effect of a small trace of an impurity is often diametrically opposite to that of a large quantity, and causes the transfer of energy to take place in the opposite direction along the spectrum. There are evidently two quite different mechanisms of interaction possible between the atoms of the two gases—a problem I commend to the chemist for investigation.

But it is not necessary to mix a gas with another gas in order to produce the energy transfer. It can be achieved otherwise, as some further slides I have here will suffice to show. We have made many measurements of intensity, more especially in the spectrum of pure helium, of the lines from a pure gas as dependent on the part of the tube they arise from, and on the conditions of excitation. We shall only consider one or two of the more interesting results which arise from a comparison of three spectra of helium: (1) the "ordinary" spectrum, or the spectrum given by the capillary of a vacuum tube containing helium at about a millimetre pressure, excited by the discharge from an induction coil without capacity or spark gap; (2) the bulb spectrum, obtained by putting a small condenser and a very small spark gap in parallel in the circuit; and (3) the capillary spectrum, with a spark gap and a strong condensed discharge. In both (2) and (3), the transfer of energy to the more refrangible members of a series takes place very strongly. In the Diffuse Series, the transferred energy goes in (3) mainly towards increased breadth of the line, but in (2) mainly towards enhanced central intensity—two very different effects. The Sharp and Principal Series show the

same transfer quite definitely, though on a smaller scale, and the effect in these series is more closely confined to enhancement of the central intensity.

The most striking enhancements produced by the condensed discharge in helium occur with the lines $\lambda 4172$ and $\lambda 4388$, which are precisely the helium lines apt to be found abnormally strong in the spectra of some of the planetary nebulae. Some other experiments we have made, on the spectrum of helium at very low pressure, indicate that these lines, together with the line $\lambda 5015$ more frequently quoted, are the strongly enhanced lines also in these circumstances. If the two sets of circumstances occur together, $\lambda 5015$ is not especially strong, but the others are enhanced for both reasons. We have in fact been able to demonstrate that the peculiar "nebular" spectrum of helium could be produced in the laboratory by a combination of the condensed discharge with an extremely low pressure.

I shall not discuss the spectra of gases as dependent, in their intensity relations, on pressure. The time required would be prohibitive, and my object is to indicate the range of work now open to precise investigation, rather than to give any complete account of the phenomena which the method has yet indicated or elucidated. One remark must, however, be made in connection with high-pressure spectra. We investigated the intensity distribution in a helium tube at the extraordinary pressure of 42 mm. Except for the trace of hydrogen which came out of the electrodes during the discharge the helium was pure. Yet the hydrogen spectrum was nevertheless predominant on the plate, and fourteen members of the Balmer series, instead of the usual seven or eight, could be seen visually as very sharp lines. This phenomenon incidentally cannot be reconciled with the current quantum theory of the hydrogen spectrum—perhaps not an unexpected fact to those conversant with the hydrogen spectrum. No spectroscopist can in fact accept a theory which can give no hint of the origin of the so-called "secondary spectrum" of hydrogen, known to arise mainly from the atom, and, in the laboratory at least, the most important and extensive part of the spectrum. The elucidation of this spectrum is in many ways the most fundamental problem of physics, and far more fundamental than the Balmer series problem. No atomic theory as yet has begun to interpret any of this spectrum, and several have given a theoretical account of the Balmer series.

Many of the new problems of interest, which the possession of an accurate method of intensity determination in spectra enables us to attack, are mainly of astrophysical importance. There may be variations of intensity in the Fraunhofer lines accompanying other more readily perceived solar phenomena, for example, but of more urgent importance is the need for a series of photographic registers of the intensity across the whole spectrum of a new star at different stages

of its history. It has not often been possible even to determine the actual number of component radiations, in an apparent broad band with a structure, emitted from such a star, at least with any real certainty. A method which automatically sifts out such bands and gives peaks on a photograph at all the maxima of intensity in the band may well be expected to contribute greatly to the elucidation of the phenomena taking place, which must in any case be totally different from anything known by our terrestrial experience.

The only other class of phenomenon depending for its elucidation on precise measures of intensity in spectrum lines, to which I shall refer with further illustrative slides, is the variation which takes place in the spectrum from a helium tube as we recede from the cathode. The slides serve to show the considerable differences which take place in the distribution of the various series, which are all emitted most strongly at unequal distances from the cathode. One very extraordinary result, indicated clearly on the last slide, is the fact that there exists a narrow region of the tube in which the characteristic spark line $\lambda 4686$ is emitted simultaneously with the helium band spectrum, a circumstance which necessitates some readjustment of preconceived ideas.

[J. W. N.]

Friday, June 6, 1919.

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PROFESSOR SIR ERNEST RUTHERFORD, LL.D. D.Sc. F.R.S. M.R.I.
(Nobel Laureate).

Atomic Projectiles and their Collisions with Light Atoms.

THE discovery of radio-activity has not only thrown a flood of light on the processes of transformation of radio-active atoms; it has at the same time provided us with the most powerful natural agencies for probing the inner structure of the atoms of all the elements. The swift α -particles and the high-speed electrons or β -rays ejected from radio-active bodies are by far the most concentrated sources of energy known to science. The enormous energy of the flying α -particle or helium atom is illustrated by the bright flash of light it produces when it impacts on a crystal of zinc sulphide, and by the dense distribution of ions along its trail through a gas. This great store of energy is due to the rapidity of its motion, which in the case of the α -particle from radium C (range 7 c.m. in air) amounts to 19,000 km. per second, or about 20,000 times the speed of a rifle-bullet. It is easily calculated that the energy of motion of an ounce of helium moving with the speed of the α -particle from radium C is equivalent to 10,000 tons of solid shot projected with a velocity of 1 km. per second.

In consequence of its great energy of motion the charged particle is able to penetrate deeply into the structure of all atoms before it is deflected or turned back, and from a study of the deflection of the path of the α -particle we are able to obtain important evidence on the strength and distribution of the electric fields near the centre or nucleus of the atom.

Since it is believed that the atom of matter is, in general, complex, consisting of positively and negatively charged parts, it is to be anticipated that a narrow pencil of α -particles, after passing through a thin plate of matter, should be scattered into a comparatively broad beam. Geiger and Marsden showed not only that much small scattering occurred, but also that in passing through the atoms of a heavy element some of the α -particles were actually turned back in their path. Considering the great energy of motion of the α -particle, this

is an arresting fact, showing that the α -particle must encounter very intense forces in penetrating the structure of the atom. In order to explain such results, the idea of the nucleus atom was developed in which the main mass of the atom is concentrated in a positively charged nucleus of very small dimensions compared with the space occupied by the electrons which surround it. The scattering of α -particles through large angles was shown to be the result of a single collision where the α -particle passed close to this charged nucleus. From a study of the distribution of the particles scattered at different angles, results of first importance emerged. It was found that the results could be explained only if the electric forces between the α -particle and charged nucleus followed the law of inverse squares for distances apart of the order of 10^{-11} cm. Darwin pointed out that the variation of scattering with velocity was explicable only on the same law. This is an important step, for it affords an experimental proof that, at any rate to a first approximation, the ordinary law of force holds for electrified bodies at such exceedingly minute distances. It was also found that a resultant charge on the nucleus measured in fundamental units was about equal to the atomic number of the element. In the case of gold this number is believed from the work of Moseley to be 79.

Knowing the mass of the impinging α -particle and of the atom with which it collides, we can determine from direct mechanical principles the distribution of velocities after the collision, assuming that there is no loss of energy due to radiation or other causes. It is important to notice that in such a calculation we need make no assumption as to the nature of the atoms or of the forces involved in the approach and separation of the atoms. For example, if an α -particle collides with another helium atom, we should expect the α -particle to give its energy to the helium atom, which could thus travel on with the speed of the α -particle. If an α -particle collides directly with a heavy atom—e.g. of gold of atomic weight 197—the α -particle should retrace its path with only slightly diminished velocity, while the gold atom moves onward in the original direction of the α -particle, but with about one-fiftieth of its velocity. Next, consider the important case where the α -particle of mass 4 makes a direct collision with a hydrogen atom of mass 1. From the laws of impact, the hydrogen atom is shot forward with a velocity 1.6 times that of the impinging α -particle, while the α -particle moves forward in the same direction, but with only 0.6 of its initial speed. Marsden showed that swift hydrogen atoms set in motion by impact with α -particles can be detected like α -particles by the scintillations produced in a zinc sulphide crystal. Recently I have been able to measure the speed of such H atoms and found it to be in good accord with the calculated value, so that we may conclude that the ordinary laws of impact may be applied with confidence in such cases. The relative velocities of the α -particles and recoil atom after collision can thus

be simply illustrated by impact of two perfectly elastic balls of masses proportional to the masses of the atoms.

While the velocities of the recoil atoms can be easily calculated, the distance which they travel before being brought to rest depends on both the mass and the charge carried by the recoil atom. Experiment shows that the range of H atoms, like the range of α -particles, varies nearly as the cube of their initial velocity. If the H atom carries a single charge, Darwin showed that its range should be about four times the range of the α -particle. This has been confirmed by experiment. Generally, it can be shown that the range of a charged atom carrying a single charge is mu^3R , where m is the atomic weight, and u the ratio of the velocity of the recoil atom to that of the α -particle, and R the range of the α -particle before collision. In comparison of theory with experiment, the results agree better if the index is taken as 2.9 instead of 3. If, however, the recoil atom carries a double charge after a collision, it is to be expected that its range would only be about one-quarter of the corresponding range if it carried a single charge. It follows that we cannot expect to detect the presence of any recoil atom carrying two charges beyond the range of the α -particle, but we can calculate that any recoil atom, of mass not greater than oxygen and carrying a single charge, should be detected beyond the range of the α -particle. For example, for a single charge the recoil atoms of hydrogen and helium should travel 4 R , lithium 2.8 R , carbon 1.6 R , nitrogen 1.3 R , and oxygen 1.1 R , where R is the range of the incident α -particles. We thus see that it should be possible to detect the presence of such singly charged atoms, if they exist, after completely stopping the α -particles by a suitable thickness of absorbing material. This is a great advantage, for the number of such swift recoil atoms is minute in comparison with the number of α -particles, and we could not hope to detect them in the presence of the much more numerous α -particles.

In order to calculate the number of recoil atoms scattered through any given angle from the direction of flight of the α -particles, it is necessary, in addition, to make assumptions as to the constitution of the atoms and as to the nature and magnitude of the forces involved in the collision. Consider, for example, the case of a collision of an α -particle with an atom of gold of nuclear charge 79. Assuming that the nucleus of the α -particle and that of the gold atom behave like point charges, repelling according to the inverse square law, it can readily be calculated that, for direct collision, the α -particle from radium C, which is turned through an angle of 180° , approaches within a distance $D = 3.6 \times 10^{-12}$ cm. of the centre of the gold nucleus. This is the closest possible distance of approach of the α -particle, and the distance increases for oblique collisions. For example, when the α -particle is scattered through an angle of 150° , 90° , 30° , 10° , 5° , the closest distances of approach are 1.01, 1.2, 2.4, 6.2, 12 D respectively.

In the experiments of Geiger and Marsden, the number of α -particles scattered through 5° was observed to be about 200,000 times greater than the number through 150° . The variation with angle was in close accord with the theory, showing that the law of inverse squares holds for distances between 3.6×10^{-12} cm. and 4.3×10^{-11} cm. in the case of the gold atom. The experiments of Crowther in 1910 on the variation of scattering of β -rays with velocity indicate that a similar law holds also in that case, and for even greater distances from the nucleus.

We have seen that Marsden was able by the scintillation method to detect hydrogen atoms set in swift motion by α -particles up to distances about four times the range of the incident α -particle. In Marsden's experiments a thin-walled glass tube filled with radium emanation served as an intense source of rays. Since the lack of homogeneity of the α -radiation and the absorption in the glass are great drawbacks in making an accurate study of the laws controlling the production of swift atoms by impact, I have found it best to use for the purpose a homogeneous source of radium C by exposing a disc in a strong source of emanation. Fifteen minutes after removal from the emanation the α -rays from the disc are practically homogeneous, with a range in air of 7 cm. By special arrangements very intense sources of α -radiation can be produced in this way, and in the various experiments discs have been used the γ -ray activity of which has varied between 5 to 80 milligrams of radium. Allowance can easily be made for the decay of the radiation with time.

In the experiments with hydrogen the source was placed in a metal box about 3 cm. away from an opening in the end covered by a thin sheet of metal of sufficient thickness to absorb the α -rays completely. A zinc sulphide screen was mounted outside about 1 mm. away from the opening, so as to allow for the insertion of absorbing screens of aluminium or mica. The apparatus was filled with dry hydrogen at atmospheric pressure. The H atoms striking the zinc sulphide screen were counted by means of a microscope in the usual way. The strong luminosity due to the β -rays from radium C was largely reduced by placing the apparatus in a powerful magnetic field which bent them away from the screen.

If we suppose, for the distances involved in a collision, that the α -particle and hydrogen nucleus may be regarded as point charges, it is easy to see that oblique impacts should occur much oftener than head-on collisions, and consequently that the stream of H atoms set in motion by collisions should contain atoms the velocities of which vary from zero to the maximum produced in a direct collision. The slow-velocity atoms should greatly preponderate, and the number of scintillations observed should fall off rapidly when absorbing screens are placed in the path of the rays close to the zinc sulphide screen.

A surprising effect was, however, observed. Using α -rays of range 7 cm., the number of H atoms remained unchanged when the

absorption in their path was increased from 9 cm. to 19 cm. of air equivalent. After 19 cm. the number fell off steadily, and no scintillations could be observed beyond 28 cm. air absorption. In fact, the stream of H atoms resembled closely a homogeneous beam of α -rays of range 28 cm., for it is well known that, owing to scattering, the number of α -particles from a homogeneous source begin to fall off some distance from the end of their range. The results showed that the H atoms are projected forward mainly in the direction of the α -particles and over a narrow range of velocity, and that few, if any, lower velocity atoms are present in the stream.

If we reduce the velocity of the α -particle by placing a metal screen over the source, it is found that the distribution of H atoms with velocity changes, and that the rays are no longer nearly homogeneous. When the range of the α -rays is reduced to 3.5 cm., the absorption of the H atoms is in close accord with the value to be expected from the theory of point charges. It is clear, therefore, that the distribution of velocity among the H atoms varies with the speed of the incident α -particles, and this indicates that a marked change takes place in the distribution and magnitude of the forces involved in the collision when the nuclei approach closer than a certain distance.

In addition to these peculiarities, the number of H atoms is greatly in excess of the number to be expected on the simple theory. For example, for the swiftest α -rays the number which is able to travel a distance equivalent to 10 cm. of air is more than thirty times greater than the calculated value. The variation in number of H atoms with velocity of the incident α -particle is also entirely different from that to be expected on the theory of point charges. The number diminishes rapidly with velocity, and is very small for α -particles of range 2.5 cm.

It must be borne in mind that the production of a high-speed H atom by an α -particle is an exceedingly rare occurrence. Under the conditions of the experiment the number of H atoms is seldom more than $1/30,000$ of the number of α -particles. Probably each α -particle passes through the structure of 10,000 hydrogen molecules in traversing one centimetre of hydrogen at atmospheric pressure, and only one α -particle in 100,000 of these produces a high-speed H atom; so that in 10^9 collisions with the molecules of hydrogen the α -particle, on the average, approaches only once close enough to the centre of the nucleus to give rise to a swift hydrogen atom.

We should anticipate that for such collisions the α -particle is unable to distinguish between the hydrogen atom and the hydrogen molecule, and that H atoms should be liberated from matter containing free or combined hydrogen. This is fully borne out by experiment.

From the number of H atoms observed it can be easily calculated that the α -particle must be fired within a perpendicular distance

of 2.4×10^{-13} cm. of the centre of the H nucleus in order to set it in swift motion. This is a distance less than the diameter of the electron, viz. 3.6×10^{-13} cm. The general results obtained with α -rays of range 7 cm. are similar to those to be expected if the α -particle behaves like a charged disc, of radius of about the diameter of an electron, travelling with its plane perpendicular to the direction of motion.

It is clear from the experiments with hydrogen that, for distances of the order of the diameter of the electron, the α -particle no longer behaves like a point charge, but that the α -particles must have dimensions of the order of that of the electron. The closest distance of approach in these collisions in hydrogen is about one-tenth the corresponding distances in the case of a collision of an α -particle with an atom of gold.

The results obtained with hydrogen in no way invalidate the nucleus theory as used to explain the scattering of α -rays by heavy atoms, but show, as we should expect, that the theory breaks down when we approach very close to the nucleus structure. In our ignorance of the constitution of the nucleus of the α -particle, we can only speculate as to its structure and the distribution of forces very close to it. If we take the α -particles of mass 4 to consist of four positively charged H nuclei and two negative electrons, we should expect it to have dimensions of the order of the diameter of the electron, supposing, as seems probable, that the H nucleus is of much smaller dimensions than the electron itself. When we consider the enormous magnitude of the forces between the α -particle and the H nucleus in a close collision amounting to 6 kg. of weight—it is to be expected that the structure of the α -particle should be much deformed, and that the law of force may undergo very marked changes in direction and magnitude for small changes in the closeness of approach of the two colliding nuclei. Such considerations offer a reasonable explanation of the anomalies shown in the number and distribution with velocity of the H atoms exhibited for different velocities of the α -particles.

When we consider the enormous forces between the nuclei, it is not so much a matter of surprise that the nuclei should be deformed as that the structure of the α -particle or helium nucleus escapes disruption into its constituent parts. Such an effect has been carefully looked for, but so far no definite evidence of such a disintegration has been observed. If this be the case, the helium nucleus must be a very stable structure to stand the strain of the gigantic forces involved in a close collision.

We have seen that the recoil atoms of all elements of atomic mass less than 18 should travel beyond the range of the α -particle, provided they carry a single charge. Preliminary experiments, in which the α -particles passed through pure helium, showed that no long-range recoil atoms were present, indicating that after recoil the

helium atom carries a double charge. In a similar way no certain evidence has been obtained of long-range recoil atoms from lithium, boron, or beryllium. It is difficult in experiments with solids or solid compounds to be sure of the absence of hydrogen or water-vapour, which results in the production of numerous swift H atoms. These difficulties are not present in the case of nitrogen and oxygen, and a special examination has been made of recoil atoms in these gases. Bright scintillations were observed in both these gases about 2 cm. beyond the range of the α -particle. These scintillations are, presumably, due to swift N and O atoms carrying a single charge, for the ranges observed are about those to be expected for such atoms. The scintillations due to recoil atoms of N and O are much brighter than H scintillations, although the actual energy of the flying atom is greater in the latter case. This difference in brightness is probably connected with the much weaker ionisation per unit of path due to the swifter H atom.

The corresponding range of the recoil atoms was about the same in oxygen, nitrogen, and carbon dioxide. Theoretically, it is to be anticipated that the N recoil atom should give a somewhat greater range than the O atom. The recoil atoms observed in carbon dioxide are apparently due to oxygen, for if the carbon atoms carried a single charge they should be detected beyond the range of O atoms.

The number of recoil atoms in nitrogen and oxygen and their absorption indicate that these atoms, like H atoms, are shot forward mainly in the direction of the α -particles. It is clear from the results that the nuclei of the atoms under consideration cannot be regarded as point charges for distances of the order of the diameter of the electron. Taking into account the close similarity of the effects produced in hydrogen and oxygen, and the greater repulsive forces between the nuclei in the latter case, it seems probable that the abnormal forces in the case of oxygen manifest themselves at about twice the distance observed in the case of hydrogen, i.e. for distances less than 7×10^{-13} cm. Such a conclusion is to be anticipated on general grounds, for presumably the oxygen nucleus is more complex and has larger dimensions than that of helium.

In his preliminary experiments Marsden observed that the active source always gives rise to a number of scintillations on a zinc sulphide screen far beyond the range of the α -particle. I have always found these natural scintillations present in the sources of radiation employed. The swift atoms producing these scintillations are deflected in a magnetic field, and have about the same range and energy as the swift H atoms produced by the passage of α -particles through hydrogen. The number of these natural scintillations is usually small, and it is very difficult to decide definitely whether such atoms arise from the disintegration of the active matter or are due to the action of the α -particles on hydrogen occluded in the source.

These natural scintillations were studied by placing the source in a closed box exhausted of air about 3 cm. from an opening in the end covered by a sheet of silver of sufficient thickness to stop the α -rays completely. The zinc sulphide screen was fixed outside close to the silver plate. On introducing dried oxygen or carbon dioxide into the vessel, the number of scintillations fell off in amount corresponding with the stopping power of the column of gas. An unexpected effect was, however, noticed on introducing dried air from the room. Instead of diminishing, the number of scintillations was increased, and for an absorption equivalent to 19 cm. of air the number was about twice that observed when the air was exhausted. It was clear from these results that the α -particles in their passage through air gave rise to long-range scintillations which appeared of about the same brightness as H scintillations. This effect in air was traced to the presence of nitrogen, for it was shown in dry, chemically prepared nitrogen as well as in air. The number of scintillations was much too large to be accounted for by the presence of traces of hydrogen or water-vapour, for the effect observed was equivalent to the number of H atoms produced by the mixture of hydrogen at 6 cm. pressure with oxygen. The measurements were always made well outside the range of the recoil nitrogen and oxygen atoms, which we have seen are stopped by 9 cm. of air.

These swift atoms which arise from nitrogen have about the same brightness and range as the H atoms produced from hydrogen, and, presumably, are charged hydrogen atoms. Definite information on this point should be obtained by measuring the deflection of a pencil of these atoms in a magnetic and electric field. The experiments are, however, exceedingly difficult on account of the very small number of the scintillations to be expected under the experimental conditions. It should be mentioned that the evidence so far obtained is not sufficient to distinguish definitely whether these are H atoms or atoms of mass 2, 3, or 4, for the range and brightness of the latter would not be very different from those shown by the H atom.

It is difficult to avoid the conclusion that these long-range atoms arising from the collision of α -particles with nitrogen are not nitrogen atoms, but probably charged atoms of hydrogen or atoms of mass 2. If this be the case, we must conclude that the nitrogen atom is disintegrated under the intense forces developed in a close collision with swift α -particles, and that the atom liberated formed a constituent part of the nitrogen nucleus. It may be significant that from radio-active data we should expect the nitrogen nucleus of atomic mass 14 to consist of three helium nuclei of mass 4, and either two hydrogen nuclei or one nucleus of mass 2.

The effect produced in nitrogen would be accounted for if the H nuclei were outriders of the main nucleus of mass 12. The close approach of the α -particle leads to the disruption of its bond with

the central nucleus, and under favourable conditions the H atom would acquire a high velocity and be shot forward like a free hydrogen atom. Taking into account the great energy of the particle, the close collision of an α -particle with a light atom seems to be the most likely agency to promote its disruption. Considering the enormous intensity of the forces brought into play in such collisions, it is not so much a matter of remark that the nitrogen atom should suffer disintegration as that the α -particle itself escapes disruption. The results, as a whole, suggest that if α -particles or similar projectiles of still greater energy were available for experiment, we might expect to break down the nucleus structure of many of the lighter atoms.

[E. R.]

Friday, January 16, 1920.

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Low Temperature Studies.

IN 1906* it was pointed out that a workable thermoscope could be constructed by taking advantage of the fact that charcoal saturated with air or other gases at a low temperature is very sensitive to radiant energy, and that the small increase of temperature produced in a 1 gramme bulb of charcoal by the approach of a candle flame expels sufficient gas to move a suitable index. As the response was obtained even though, in the forms of apparatus then employed (Fig. 1), the radiation had to traverse several thicknesses of glass before reaching the charcoal, it was inferred that a still more sensitive thermoscope could be constructed if the receptacle containing the charcoal were closed by a thin membrane of stretched india-rubber, which is more transparent to heat than glass. Such a membrane being practically impervious to most gases at low temperatures,† it appeared possible to make the receptacle air-tight.

This arrangement was tried with the charcoal in a metal capsule covered with a very thin clear membrane, as described in the diffusion experiments of 1915.‡ The tube from this cell led to a small liquid manometer. The cell was immersed in liquid air with the clear membrane directed vertically upwards, and the charcoal was allowed to saturate with clean air up to atmospheric pressure. Covering the membrane was a light metal shutter. When everything had become equilibrated, the shutter was lifted, thus exposing the cell to radiation from any source above and in line with the neck of the silvered vacuum vessel. With a Leslie cube at room temperature as source, an immediate response was obtained, sufficient to displace the index of the manometer to the limit of its scale in a few minutes. On replacing the shutter the opposite effect was obtained, as the charcoal re-absorbed the gas displaced by the dark radiation.

In addition to rubber membranes, plates of rolled silver chloride

* Proc. Roy. Inst., xviii. p. 415.

† Proc. Roy. Inst., xvii p. 424; xxi. pp. 558, 816.

‡ Proc. Roy. Inst., xxi. p. 558.

and polished rock-salt were successfully employed, both these substances being very transparent to dark heat rays.

These results were demonstrated as follows :—

(1) *Heat transference through a thin membrane.* In the parallel beam from an arc lamp was placed an unsilvered glass spherical vacuum vessel, 5 to 6 inches diameter, filled with filtered liquid air. In the focus of the rays thus obtained pieces of black paper were readily ignited. The same result followed when a thin membrane of stretched india-rubber was interposed, as also with a plate of polished

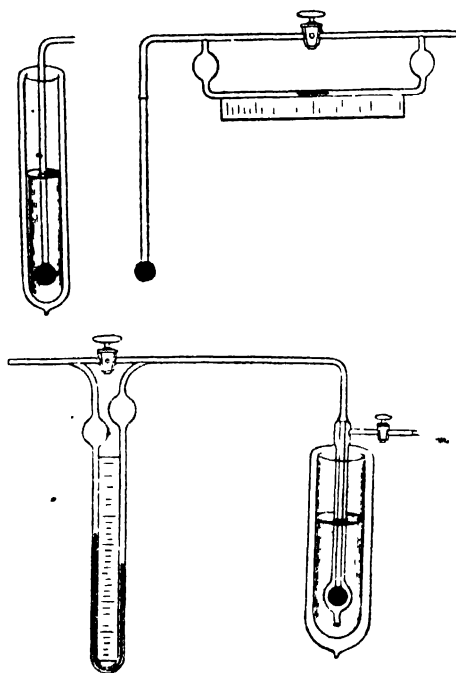


FIG. 1.

rock-salt. With an india-rubber membrane less stretched, and therefore thicker and not so clear, there was difficulty in getting the paper to glow, while a dull and still thicker membrane absorbed the bulk of the heat, and no appreciable effect could be obtained.

When a pad of wool soaked in liquid air was drawn across a stretched rubber membrane, puckering was produced by the expansion of the india-rubber. The opposite effect was demonstrated by means of an india-rubber balloon distended by water, and supported in a large glass funnel. By carefully pricking the balloon with a

fine needle, a steady jet of water was obtained, the upper limit of which was projected on the screen. On pouring warm water over the balloon, the resultant tightening of the rubber was shown by a sudden rise in the height of the water jet.

(2) *Elasticity of rubber membrane in liquid air and at ordinary temperatures.* An empty metal capsule 4 cm. diameter, covered by a membrane, was connected to a U-manometer, and its scale projected on the screen. A 5 cm. light watch glass rested on the membrane without appreciable distortion. When loads increasing up to 200 grammes were placed on the watch glass, corresponding displacements of the manometer were obtained, increasing uniformly up to 15 cm. pressure (alcohol). This experiment was repeated after cautiously and gradationally cooling the capsule in liquid air. The

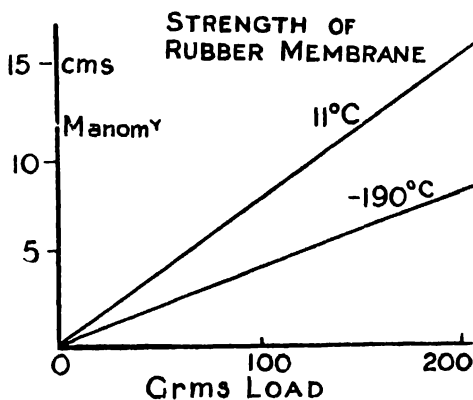


FIG. 2.

resulting displacements for the same loads reached only 8 cm., but were still quite regular, as shown in Fig. 2.

(3) *Membrane impervious at low temperatures.* This experiment was first shown in the Discourse of June 5, 1908.* An india-rubber membrane was stretched and bound over the end of a piece of glass tube about 2 cm. diameter, to which was sealed an ordinary discharge tube and charcoal bulb with stopcock. The membrane was cautiously cooled and immersed in liquid air, and the apparatus was exhausted by opening the charcoal stopcock. The vacuum was then too high for a discharge to pass, and remained so when the charcoal was shut off. When the membrane was cautiously warmed up by steadily lowering the liquid air vessel in which it was immersed, air began to pass through the membrane and the discharge started.

* Proc. Roy. Inst., xix. p. 417.

On re-cooling the membrane and opening the charcoal, the pressure was quickly reduced and the former high vacuum restored.

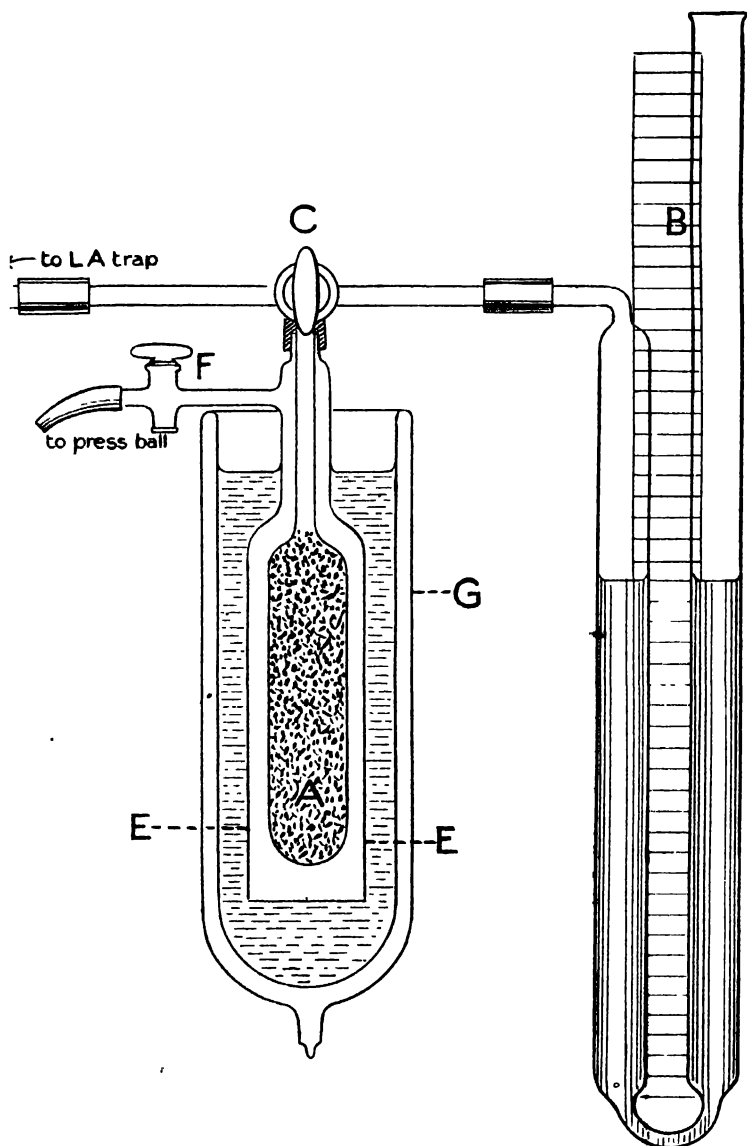


FIG. 3.

(4) *Action of a large charcoal thermoscope.* Instead of the small 1 gramme charcoal bulb (Fig. 1) and projected manometer shown on June 8, 1906, a cylindrical bulb A (Fig. 3), containing 80 grammes of charcoal, was connected to a manometer B, of which the limbs were 2 feet high. The bulb A was immersed in liquid air to saturate the charcoal to atmospheric pressure with clean dry air. A 3-way stopcock C at the top of the charcoal bulb A gave connection either to the manometer or to a liquid air trap (not shown) to clean the air before being condensed. An annular tube E, open at the bottom, covered the bulb, and was connected airtight above by rubber tubing. An opening with a stopcock F led to a press-ball, by means of which the liquid air could be forced out from the annular space round the charcoal bulb. The vacuum vessel G, in which the arrangement was immersed, was silvered half-way round, the remainder being clear; hence, when rotated, it screened off the radiation directed upon the charcoal from the front.

A dispersed beam 3 feet broad, from an arc lamp a yard away, was used to illuminate and actuate the thermoscope. With the silvered half of the vacuum vessel towards the lantern, and C turned to connect A to the manometer, the movement of the liquid was scarcely perceptible; but when the charcoal was exposed through the unsilvered glass, a displacement of 30 cm. in 15 seconds resulted, the annular space being full of liquid air. When this was emptied by the press-ball connected to F, the displacement in the same time was over 60 cm.

MEASUREMENTS OF TRANSMISSIVE POWERS.

In the cell employed for laboratory measurements the sensibility depends finally on the degree of relative isolation between the saturated charcoal and the liquid air or oxygen of the bath. If the charcoal is in close contact with the cell walls, the absorbed radiation is unable to raise the temperature of the charcoal sufficiently to affect the manometer to any extent; in the other extreme, not only are the initial displacements more erratic, but the time taken to re-equilibrate is too great. An arrangement that is very sensitive and quite workable is to lower the level of the liquid in the bath below the cell, but the space above the liquid must then have a very small temperature gradient. This condition can be secured by efficient cooling of the enclosing walls, as in the gas or air-cooled cell (see below).

The principal application of the arrangement was for measuring the relative absorptions of infra-red radiation up to 100°C. , exhibited by a great number of substances when immersed in the form of plates of various thicknesses in the liquid air above the cell. The proportionate absorption was determined by two successive readings with the shutter raised for $\frac{1}{2}$ to 1 minute to expose the cell to a

Leslie cube, the cell being unscreened for the first measurement, while for the second a plate of known thickness (down to a fraction of a mm.) of the material to be examined was placed on a light stage

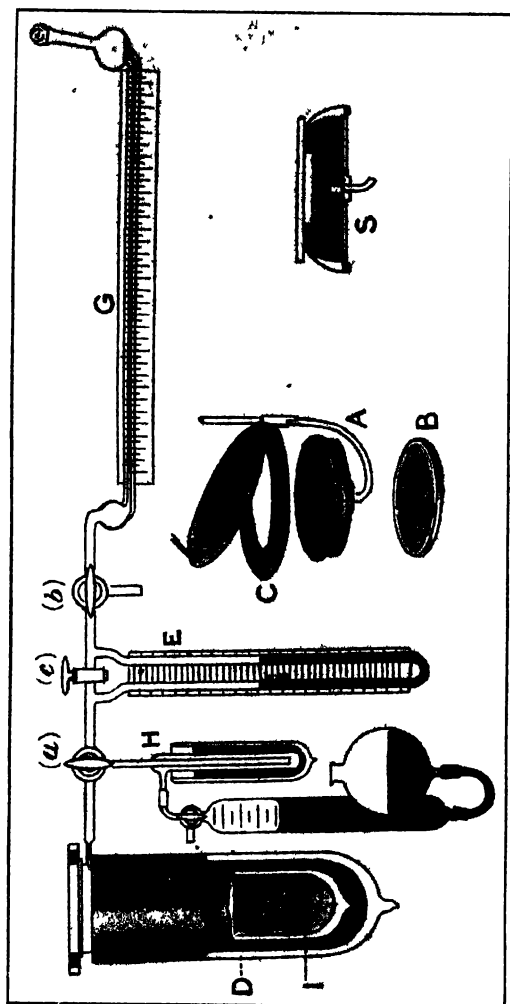


FIG 4—GENERAL ARRANGEMENT OF THERMOSCOPE

above the membrane. Usually two sets of observations were made with the Leslie cube, one at room temperature and the other at 100°C . - Some lower temperatures were tried with interesting results.

The working arrangement is shown in Fig. 4. Details of the

cell are shown at A. The metal capsule is covered by a transparent rubber membrane through which can be seen the tray of charcoal. This tray (shown separately at (B) below) was a tambourine of chiffon gauze, stretched by a pair of light brass rings of square section. A thin layer of clean dry absorptive charcoal—less than 1 gramme, in pieces of about $\frac{1}{2}$ mm.—was spread on the tambourine, which fitted loosely into the capsule; the charcoal was thus kept free in the cell space. The shutter above the cell was a simple hinged brass lid actuated by a light chain of silver or softened platinum wire, running through eyes and over a small pulley above (not shown). The lid, when closed, rested on a flat ring platform C, carried by a sleeve fitting on a thin (1 mm. bore, $\frac{1}{2}$ mm. walls) german silver tube leading out from the bottom of the cell. The plates of material whose transmissivity was to be measured were placed on the platform, the shutter being hollowed out sufficiently to allow this.

The form of the cell employed for plates of silver chloride or rock-salt is shown at S. The wall of the cell was a spherical segment of pure assay lead about $\frac{1}{2}$ mm. thick soldered to a brass disc as base, from which the thin german silver tube led to the manometer. The silver chloride (or rock-salt) plate was luted to the upper rim of the lead, which was flattened to receive it. The interior of this cell was occupied by an ebonite block, hollowed out above to contain the charcoal, as in the metal cell, and with a small opening below, to connect to the exit tube. The upper surface of the ebonite fitted under the lead rim, without being luted to it, as the contractions of lead and ebonite differ so considerably at low temperatures that otherwise there would be a tendency to crack the plate. Thus the lead rim was left free to follow the contraction of the rock-salt plate.

In a later form of cell the lead shell was soldered to a brass ring below, slightly coned to fit a similar ring on the periphery of the brass base plate. The ebonite was then used only for the first shaping of the lead rim, and the charcoal was supported in the lower half of the cell, as in the metal capsule already described. This arrangement allowed either charcoal or membrane to be altered as required without mutual disturbance.

The cell was immersed in liquid air (or oxygen or nitrogen, etc.) in the inner of two vacuum vessels (shown at D and I) arranged in the usual way for good isolation. The thin german silver tube led from the cell to a wider tube in connection with the manometers E and G. Two three-way stopcocks (*a*) and (*b*) were inserted on each side of manometer E, which itself had a plain stopcock (*c*) closed only when it was registering. The third connection of (*a*) was sealed to a liquid air trap H, of the usual annular form, leading to the supply of gas used to saturate the cell charcoal. With liquid oxygen or old liquid air in I, room air was good enough for this purpose; but nitrogen, hydrogen and helium were all employed in

testing the behaviour of the cell under different circumstances at different temperatures, as was also carbonic acid.

While the cell was being saturated, or settling between readings, stopcock (*a*) was set as shown—i.e. open to the gas reservoir at constant pressure, or open to the atmosphere; (*b*) was also in the same position as (*a*) open to the air (generally through a small drying bulb of fresh soda lime). When a reading was to be taken on E, (*c*) was closed, and (*a*) turned to connect the cell to the manometer only. A blank reading was then made, with the cell shutter closed, to test for equilibrium in the cell. The "zero" of the instrument, thus taken, did not exceed 2 or 3 mm. displacement, and usually was of the order of 1 mm. or less: (*a*) and (*c*) were then once more opened to equilibrate everything. In order to make an observation the cock (*c*) was closed, and the shutter raised before turning (*a*) to connect with the manometer E. (This was to avoid the fluctuations of pressure caused by eddies in the liquid due to the moving shutter and transmitted through the elastic membrane.) The stopcock (*a*) was then turned as before, and at the same moment the stopwatch was started. At the end of $\frac{1}{2}$ minute (or whatever the period required) (*a*) was reversed to open the cell to H, etc., and close the connection to the manometer E. The shutter was then lowered and the cell left for about 10 minutes to equilibrate. The manometer liquid remained in its displaced position until (*c*) was again opened, thus allowing ample time for the reading to be taken. In the same way for readings on the horizontal manometer G, (*b*) was turned to the position shown, with (*a*) set as first described; (*c*) remained open, and the reading was taken as before by turning (*a*) at the same time as the stopwatch was started, after raising the shutter.

In Fig. 5 are shown three alternative arrangements of cell and bath in more detail than is possible in Fig. 4. They consist essentially of inner and outer vessels (charged with liquid air or nitrogen, oxygen, etc.), the only purpose of the outer one being to arrest heat influx to the inner one, and thus to reduce to a minimum any fluctuations of the temperature of the cell immersed therein. The inner vessel of A, Fig. 5, with a straight central tubular outlet below was constructed of quartz, for the purpose of supporting the thin metal tube connecting the cell to the manometer; this arrangement left the whole space above the membrane free from obstruction. The vacuum isolation of this vessel did not extend up beyond two-thirds of its height, thus allowing the outer liquid air to maintain complete contact, and ensuring a uniform temperature throughout the inner vessel. The upper part should preferably be conical in shape, in order to cut off the radiation from the uncooled parts which otherwise would affect the cell when the shutter was raised. The simple shutter shown was lifted vertically for an exposure (the outer portions of the cell being covered with a ring diaphragm); but a properly hinged shutter was also used, fixed to a light sleeve fitting

into the vacuum vessel above the cell. An annular space filled with charcoal formed part of the construction of the quartz vessel, to ensure the maintenance of highest vacuum isolation at low temperature. Since the metal connecting tube of the cell passes through the liquid in the outer vessel, it is necessary that the liquid air used there should be of the same temperature and composition as that in the inner vessel. The safest procedure is to have liquid oxygen in both.

The simpler form shown in B was commonly employed, and was

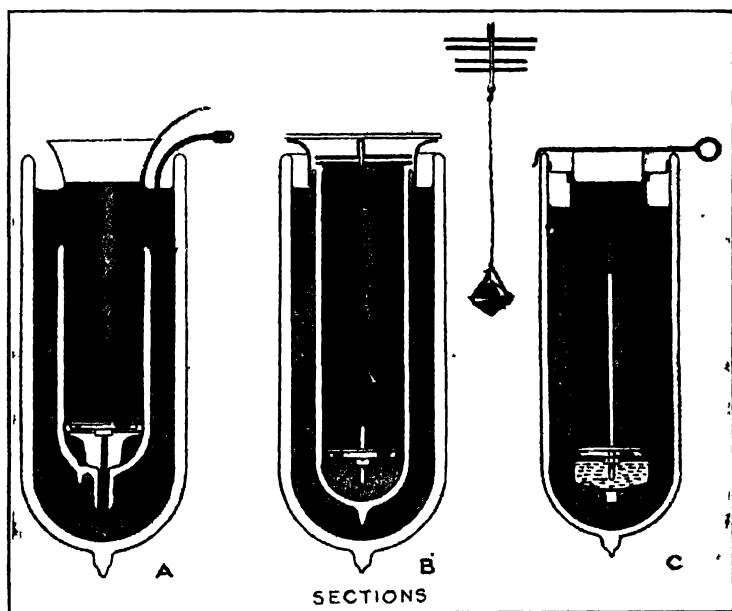


FIG. 5.—FORMS OF CELL.

the most simple to use for transmission measurements. Both inner and outer vessels were of the silvered cylindrical type. The isolation of the inner by the cooling of the outer was not so effective as in A, but was reinforced by the use of a set of thin polished metal discs with an axial support of an ebonite or thin german silver tube (closed at the ends). This device very effectively reduced the radiation and convection losses consequent upon the open unprotected neck. In addition a light sheet metal hood and cover plate were fixed to the neck to protect it from disturbance when opened. Attached by thread to the disc stopper was some uranium nitrate,

shown in the diagram as a single crystal, but small crystals were commonly used in a chiffon gauze bag. This substance becomes electrified at low temperatures with the slightest friction, and effectively removes floating crystals of ice or other impurities, thus keeping the liquid air perfectly clear. It becomes moist in use after some time, and care must be taken not to dehydrate it when drying, as it would then become inoperative.

The cell and tube are shown only in part (the tube being bent under and passing up behind the cell), and the trap door, etc., are omitted. With the most effective internal cooling, the trap door can be omitted, since the disc stopper, if well polished, almost completely cuts off external radiation. The drawback to this form is the stray radiation from the upper portion of the inner wall, whose temperature cannot be kept steadily down to that of the liquid bath. A lining of black bibulous paper or thin blackened sheet copper is of assistance, but does not eliminate the difficulty in such a vessel, which has to be opened intermittently during use.

Some of these drawbacks are eliminated in C, which was afterwards developed almost into a standard form. The inner vessel holds a separate small quantity of liquid, but being of plain metal is unisolated, and takes throughout the uniform temperature of the liquid in the outer vessel, which extends farther above the top of the inner vessel than the diagram indicates. The top is closed by a light metal cup fitting with the minimum of play; into this is placed some of the same liquid air as is used in the vessels. A uranium bag can be attached below, as with the disc stoppers, but in the figure the cell is shown "gas cooled," i.e. above the liquid in the inner vessel. A light cross support serves as a handle to remove this "bucket" stopper for an exposure. It is of course supported meanwhile in a suitable glass vacuum vessel of liquid air. The objection to this form, apart from the need of rather frequent replenishment of the bucket, is the cloud which sometimes forms when the atmosphere is moist, or if the bucket is lifted too rapidly. But with careful use very good results are obtained.

CURVES OF DISPLACEMENT OF GAS WITH TIME.

The evolution of air or gas from the cell, as revealed by time and displacement curves, showed only a small departure from a linear rate for 2 or 3 minutes. After this the gas was expelled more slowly, and in from 10 to 15 minutes the manometer had almost stopped. Two manometers were used. The first was the ordinary U-tube form, to register the rate of growth of pressure; while in the second the rate of gas evolution at sensibly constant pressure was indicated on a horizontal scaled tube, with a bulb reservoir at the end furthest from the cell. In this form the linear character of the earlier displacement range continued longer than the ordinary U-tube, and

the time taken for settling, after an exposure, was less, since the gas equilibrium in the charcoal was not so much disturbed as when the pressure was raised.

The relative displacements resulting from the "gas-cooled" cell, as compared with those from the "liquid-cooled" cell (cell all

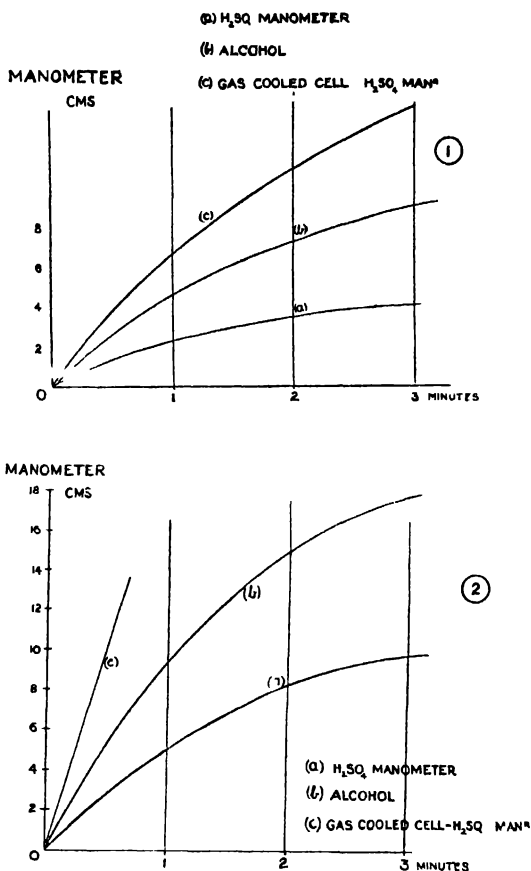


FIG. 6 —VERTICAL MANOMETER, 1, 15° C. RADIATION, 2, 100° C. RADIATION.

immersed) are included in the curves, Figs. 6 and 7, which show how the readings grow with continued exposure. Separate curves for radiation from a Leslie cube at 15° C. and 100° C. respectively are given, also comparative readings with either alcohol or sulphuric acid in the manometers. (Later petroleum was used, fractionated

between 125°C. and 140°C. , and tinted with "scharlach-R." This, though as light and mobile as the alcohol, gave no vapour which by condensation might choke the narrow tubes of the thermoscope; the more viscous and dense sulphuric acid could then be dispensed with.) Half to 1 minute was the usual period of exposure when comparing fluxes of radiation, the displacements with the same aperture in

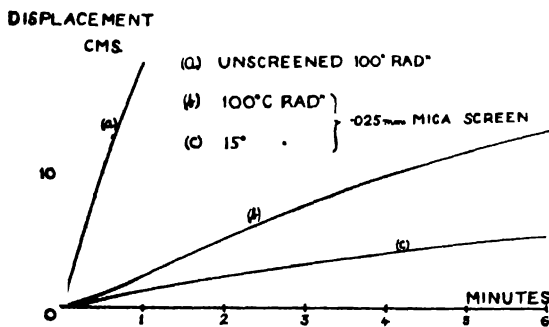
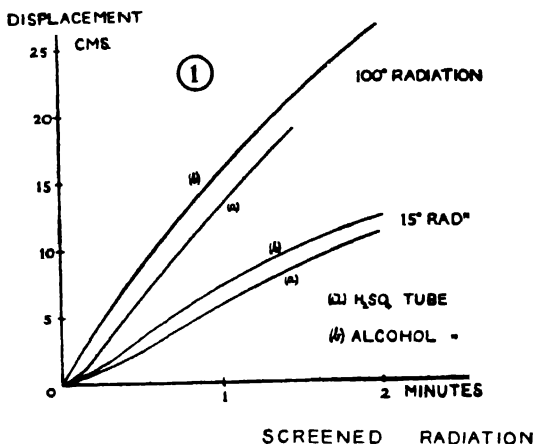


FIG. 7.—HORIZONTAL SCALED TUBE.

equal times being then compared; when the inertia of the liquid caused any initial distortion, the first 5 or 10 seconds were not counted. A longer period was advisable when a very absorptive screen gave low readings. The curve (Fig. 7 (2)) shows this in the case of mica, with which readings were continued for several minutes without the occurrence of serious bending in the plotted results, as the volume of gas expelled was still quite small. In this way the

necessary accuracy, which 1 minute readings would not secure, was attained. The time taken to re-equilibrate after such a reading is no longer than is necessary after an ordinary $\frac{1}{2}$ to 1 minute's exposure to unscreened radiation, as the volume of gas expelled is no greater.

It was not intended, with such a cell, to get absolute measurements, because, as already seen, the charcoal is only partially isolated; hence only comparative measures were taken, everything being related to the unscreened radiation from the black Leslie cube at ordinary temperature, taken on each occasion for comparison.

When exposed, therefore, to a uniform flux of radiation, the absorbed gas will be liberated up to a steady limit defined by the small maintained increment of temperature of the charcoal above that of the bath. Directly the radiation is shut off, by lowering the

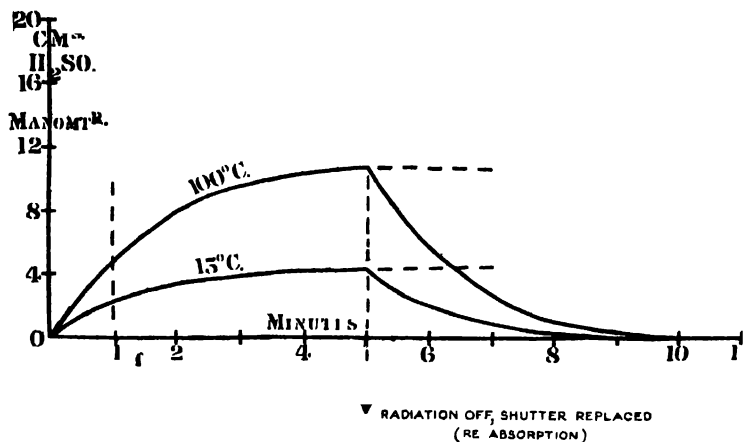


FIG. 8.

shutter over the cell, the charcoal again falls to the original temperature, and the expelled gas is re-absorbed. The general character of the curve is shown in Fig. 8.

An approximate idea of the possible sensibility may be gathered from a knowledge of the latent heat of gases in cooled charcoal. Thus a measurement made with 300 cc. of oxygen in 1 gramme of charcoal gave for a lowering of temperature from 90.23° Abs. to 83.2° Abs. a change of occlusion pressure from 1.0634 mm. to 0.2029 mm., i.e. a dp of 0.8605 mm. for a dT of 7.03° , or 0.123 mm. Hg. per 1° . This on a sulphuric acid manometer would be 0.905 mm. per degree.

Assuming, then, that the latent heat of the oxygen in charcoal would, at the saturation pressure of one atmosphere, be the same at

the same temperature as at the lower pressure of 1.06 mm., we should have—

$$\frac{T^2}{p} \frac{dp}{dT} = \frac{T^2}{p'} \frac{dp'}{dT}, \text{ giving } \frac{dp'}{dT} = \frac{p'}{p} \times 0.905 = \frac{760}{1.06} \times 0.905$$

= 648.8 mm. of sulphuric acid per degree.

Since the indication of the sulphuric acid manometer with the charcoal thermoscope was frequently of the order of 3 cm. for $\frac{1}{2}$ minute's exposure to a Leslie cube at 15° C., the corresponding rise of temperature would therefore be 0.05° Abs.

The measured evolution of gas at constant pressure on the horizontal scaled tube under the same circumstances was about 0.4 cc. Now, taking the thermal evolution of oxygen in charcoal as 3146 calories per gramme molecule,* corresponding to approximately 7.2 cc. evolved per calorie absorbed, the thermoscope registered 1/20th of a calorie for $\frac{1}{2}$ minute's exposure. This corresponds approximately to 56.6 mm. displacement in the scaled tube of 3 mm. bore, so that each mm. represented approximately 0.001 calorie. For more exact measurements of smaller transmissions a tube of less diameter was used.

The maximum evolution of gas corresponding to the theoretical total emission from the black body was not usually obtained, but the proportion registered was higher with small disturbances and lower with exposures to more intense radiations. Two typical cases may be quoted. In the first, the cell was exposed in the ordinary way at the lower end of a cylindrical vacuum vessel with black absorptive walls; while in the second, the walls were made reflecting with a lining of thin polished metal. In the first case the cell was distant 18 cm. from the open neck covered by a black cube at 15° C. Now, with cell $2\frac{1}{2}$ cm. diameter (4.9 cm.² area) 18 cm. below the neck, of diameter $5\frac{1}{2}$ cm. (neck area = 23.7 cm.²), theoretical calories diffused through vessel from a black cube at 15° C., covering the whole open neck, and absorbed at 90° Abs. (see Fig. 13):

$$= 1.374 \times 10^{-12} (288^4 - 90^4)$$

$$= 0.00945 \text{ calorie per second per cm.}^2.$$

Therefore total flux from exposed area of 23.7 cm.² = 0.2245 calorie per second, or 13.47 calories per minute.

These 13.47 calories per minute may be regarded as spread out over a hemisphere of 18 cm. radius, i.e. over an area of 2036 cm.², of which surface the cell occupies 4.9 cm.²; and will therefore absorb 4.9/2036 of the total radiation, viz. 0.032 calorie per minute. If

* Derived from a Rankine formula $\log p = A - B/T$, where B was found by experiment to be 684, whence the value of $\frac{T^2}{p} \frac{dp}{dT} = 2 \times 684 \times \log 10 = 3146$. (Proc. Roy. Inst., xix. p. 416.)

all this is utilised by the charcoal as latent heat of evaporation of the absorbed air (approx. 8 cc. evaporated per calorie) the volume of gas evolved would be 0.256 cc.

In the same way the theoretical amount from the same black cube at 100° C. would be 38 calories per minute, entering the neck, of which the cell could absorb 0.091 calorie, equivalent to a gas evolution of 0.784 cc. In both cases the absorption in the membrane over the charcoal reduces this to approximately 80 per cent. The maximum gas evolution would therefore be of the order of 0.63 cc. per minute with the black cube at 100° C., and 0.22 cc. with the cube at 15° C. The observed values in one case were 0.34 cc. at 12° C. and 0.956 cc. at 100° C. There was, however, some additional radiation from the upper region of the walls of the vacuum vessel which the cooling liquid did not reach.

When, instead of a black lined vacuum vessel, a polished lining was used, practically all the radiation should reach the cell—namely, 2.68 calories per minute from a cube at 15° C., and 7.58 calories from a cube at 100° C., equivalent respectively to 21.44 cc. and 60.65 cc. of evaporated oxygen per minute. This however should be reduced, not only by the 20 per cent. absorption of the membrane, but also by at least 15 per cent. loss on reflection from the metal (assuming only single reflection, whereas much of the radiation will be several times reflected before reaching the lower end of the cylinder). This would give a maximum theoretical evolution of 14.6 cc. per minute from the cube at 15° C., and 41.2 cc. per minute from the cube at 100° C. This evolution would disturb the gas equilibrium in the cell too much, but 10 seconds' exposure gave measures at the rate of 3.8 cc. per minute for the 15° C. exposure and 9.0 cc. per minute for the 100° C. exposure—i.e. about one-fourth of the theoretical. This sufficiently indicates the increasing lag with increasing intensity.

The response of the cell to known small increments of temperature afforded another means of studying this question. A simple method was to increase by a small measured amount the pressure under which the liquid air was evaporating from the bath in which the cell was immersed. A manometer, similar to that employed for the radiation measurements, was connected to the closed vacuum vessel, and an outlet tube was arranged at different measured depths in an open vessel of mercury, sulphuric acid, or alcohol, according to the plus pressure required. In this way an increase of temperature of the liquid air amounting only to a few hundredths of a degree was obtained, and the consequent rise of temperature of the cell was observed by the movements of the manometer attached to it. The equilibrium of different gases in the charcoal was also studied, and information obtained as to the application of oxygen, nitrogen, hydrogen, helium, etc., to the purposes of a low temperature charcoal thermoscope.

A fairly direct calibration of the instrument can thus be made in terms of actual temperature increase. Since at the boiling point of liquid oxygen the dp/dt per 1° is 81 mm. Hg., an added pressure of 14 to 15 mm. of alcohol (0.8 mm. Hg.) would correspond to an increment of temperature of the liquid air or oxygen of 1/100th degree. The curves (Fig. 9) give the indications of the thermoscope following increments of pressure of 5, 10, 15, and 20 cm. of the alcohol manometer, the corresponding increments of temperature of the liquid oxygen being 0.023° , 0.067° , 0.10° , and 0.133° Abs. The response of the thermoscope with time after these instantaneous additions of pressure to the oxygen bath are seen to be of the same character in the case of air-saturated charcoal as those produced

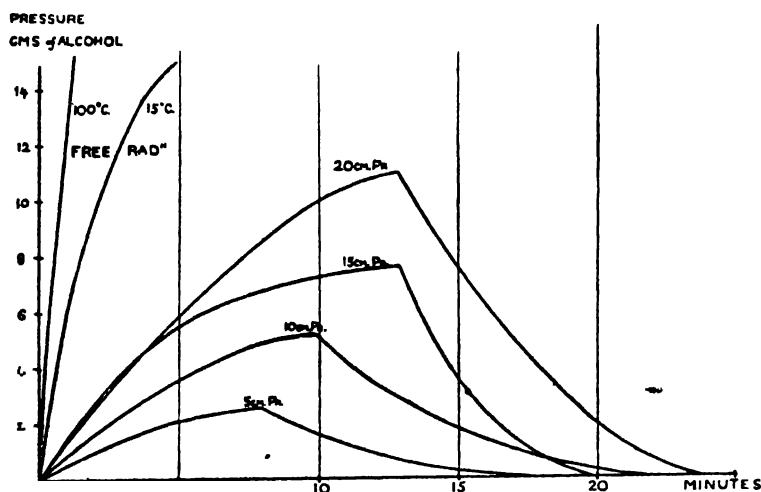


FIG. 9.—AIR SATURATION.

by the usual exposure to the Leslie cube, but of much less intensity, as shown by the comparison curve of the ordinary exposure. The limit registered by the thermoscope was in all cases less than that of the bath, as was to be expected from the higher latent heat of the air-in-charcoal as compared with the liquid oxygen. Thus the 5 cm. increment (0.033°) caused a rise of the thermoscope manometer to 2.6 cm. in 8 minutes, which on releasing the pressure of the liquid oxygen fell to 1 cm. in $3\frac{1}{2}$ minutes, and took 9 or 10 minutes to re-equilibrate to zero. Similarly for the other increments of 10 cm., 15 cm. and 20 cm. More extended measurements on these lines would no doubt give much information concerning the latent heat of gases in charcoal under various conditions.

With hydrogen saturating the charcoal instead of air (Fig. 10)

the limit was reached under the same circumstances in about $1\frac{1}{2}$ minute, and with helium (same figure), which of course is scarcely condensed at all at this temperature, the response was almost all registered in $\frac{1}{2}$ minute. These two results show incidentally that the temperature lag of the bath must be very small. For comparison here, also, the corresponding normal thermoscope responses to the Leslie cube are shown in separate curves.

All these results were the same, whether made on the membrane cell or on the silver chloride cell, so that no distortion of the

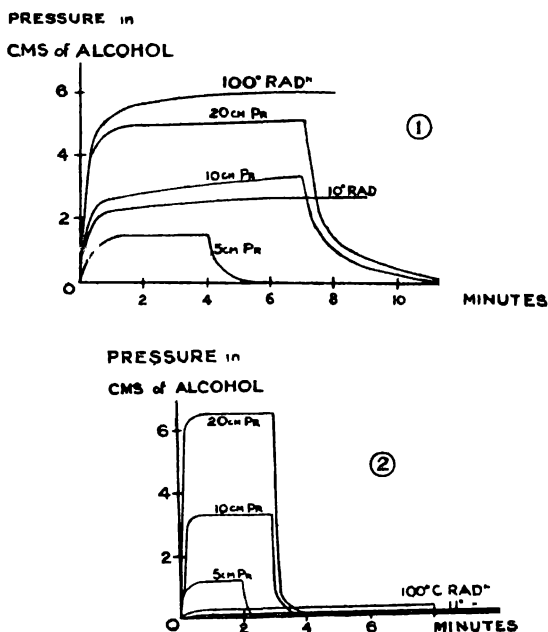


FIG. 10.—CHARCOAL SATURATED WITH (1) HYDROGEN, (2) HELIUM.

membrane under small differences of pressure will explain them. On the other hand, if no charcoal is present in the cell some effect can be detected from this cause, but the response is in all cases registered instantaneously. The curves in Fig. 11 give this response for different increments up to 20 cm. This pressure was calculated to correspond to a load of 180 grammes weight on the membrane. The response of the manometer, on the other hand, due to the stretching of the membrane, corresponded to a load of only 72 grammes, or a pressure of 8 cm., and so on for lower values. In this figure is also included the response obtained by an ordinary exposure, which

is seen to be negligible. Comparison distortions of the membrane by weight at ordinary temperatures and in liquid air have already been described.

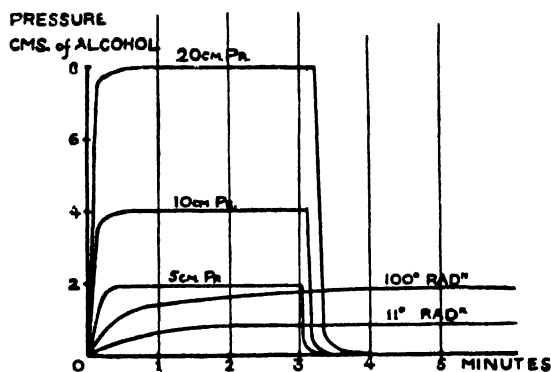


FIG. 11 — CELL WITHOUT CHARCOAL.

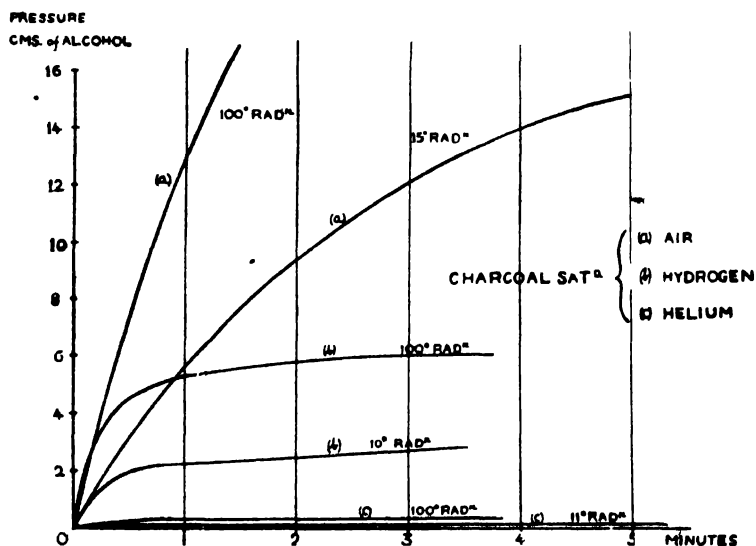


FIG. 12

Curves comparing the sensibilities of the cell when the charcoal is saturated at liquid air temperature with air, hydrogen and helium respectively are collected in Fig. 12.

COMPARISON WITH RADIATION LAWS.

As already stated, the observed proportions between the manometer readings in some unit period were the basis on which the relative amounts of radiation transmitted were estimated. In order to test the validity of this interpretation, the results so obtained were compared with the theoretical values resulting from applying the fourth power law of Stefan. The ratios from black bodies at T_1 and T_2 respectively into a liquid oxygen "sink" at 90° Abs., are thus expressed as

$$\frac{T_1^4 - 90^4}{T_2^4 - 90^4}.$$

Such ratios for certain common values of T_1 and T_2 are set out in Table I. Typical temperatures are given in columns 1 and 2, and the calculated ratios in column 3, while column 4 contains the average values obtained from the thermoscope measurements. These

TABLE I.— $(T_1^4 - 90^4)/(T_2^4 - 90^4)$ GIVES THE RELATIVE ENRGY FLUX FROM TWO TEMPERATURES, T_1 AND T_2 , INTO LIQUID OXYGEN "SINK."

T_1	T_2	Relative Flux	
		theory	Observed
100° C.	15 C.	2.83	2.6
100 "	-78 "	14.0	12.9
15 "	78 "	4.94	4.8
100 "	0 "	3.52	3.4
0 "	-78 "	3.98	3.7

ratios may be deduced directly from such a curve as that given in Fig. 13, where the values of $(T^4 - 90^4)$ are given as ordinates with T as abscissa up to $T = 373^\circ$ Abs., the higher position of the curve being shown separately with scale of ordinates to the right.

For test observations all stray radiation into the cell was either reduced as far as possible by screens or else directly measured and corrected for, by covering the vessel with a basin containing liquid air and making a "blank" exposure. For ordinary measurements of transmissivity through various materials a little stray internal radiation was not regarded as serious, as it had all to pass through the material under examination before being registered. The proportional transmission of the whole mixed radiation was therefore recorded. The principal temperatures used for the Leslie cube (or its equivalent) above the vessel (for the test measurements) were boiling water, room temperature of 10° to 15° C., melting ice and solid carbonic acid finely pounded, moistened with alcohol and

settled to a steady boiling point in an enclosed vessel. (It is very easy for solid carbonic acid to fall to a temperature considerably below its boiling point, by forced evaporation due to mere exposure to the strong air convection currents arising from free exposure of such a cold substance.) Besides this, a set of measurements at gradationally lowered temperatures between 0° and -78° C. was made, using a cooled alcohol bath as source. Measurements much above 100° C. were not satisfactory—e.g. the use of a source of boiling sulphur produced too violent a disturbance and did not give satisfactory values ; but, on the other hand, the difference between old

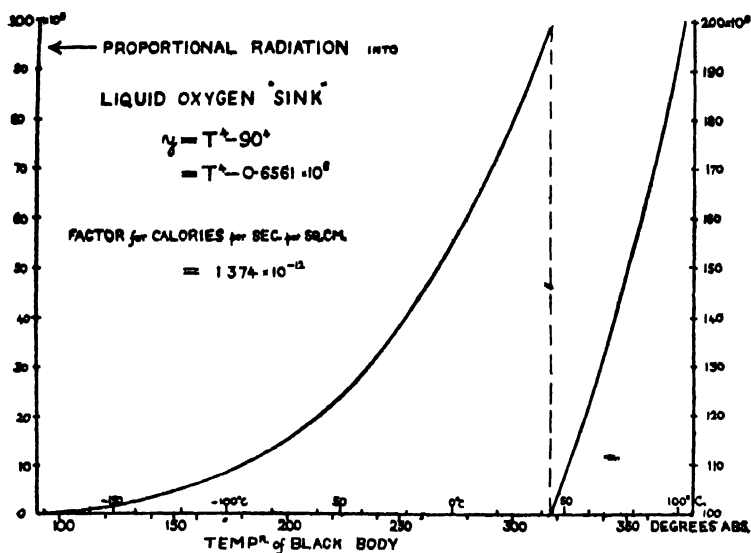


FIG. 13

and new liquid air, say at 89° Abs. and 82° Abs. respectively, was easily registered, either plus or minus as the case might be ; and also that between boiling oxygen and boiling nitrogen (90° Abs. and 77° Abs. respectively). No observations were made with liquid hydrogen, either as "black" source (negative) or to cool the thermoscope (hydrogen saturated charcoal), with a suitable Leshe cube of liquid oxygen or nitrogen as black body above, but there is no reason to doubt that this could be arranged satisfactorily. Among other questions the transmissivity for heat of liquid hydrogen could thus be tested.

TYPICAL RESULTS OF TRANSMISSIVE POWER.

Table II. exemplifies the simplest manner of deducing the proportionate transmissions of typical substances. These substances are enumerated in the first column, and their thicknesses in the second; the third and fourth columns give the actual displacements of the manometer, in two sets, with the "black body" at 15° C. and 100° C., and the fifth column gives the proportionate transmissions, based on the readings given in the first line with unscreened radiation. The first two substances were equally transmissive at several thicknesses.

TABLE II.—LIQUID AIR THERMOSCOPE OBSERVATIONS.

Solids	Mm.	Manometer		Transmissions per cent.
		15° C.	100° C	
		cm.	cm.	
		4.8	12.7	100
Rock salt . . .	3.8	4.4	11.7	92
Silver chloride . . .	1.0	4.1	10.8	85
	0.15	4.2	10.9	86
Rubber . . .	0.6	0.2	0.5	4
	0.1	1.6	4.2	38
	0.02	8.75	10.0	78
Crystalline quartz . . .	2.3	0.75	2.0	16
	1.0	0.5	1.3	10
Glass . . .	0.125	0.9	2.3	18
	0.012	1.8	4.7	37
	0.10	0.2	0.5	4
Mica . . .	0.062	0.4	1.0	8
	0.013	1.6	4.2	33
Fused quartz . . .	1.5	0.55	1.5	12

The next, rubber, became very absorptive by the time a thickness of 0.6 mm. was reached, although very transmissive when stretched to the form of a transparent membrane 0.02 mm. thick. Crystalline quartz 2.3 mm. thick was more transmissive than fused quartz of 1.5 mm.—viz. 16 per cent. and 12 per cent. respectively. Glass, even thinner than the rubber membrane, was still able to absorb two-thirds of the incident radiation, and the absorption of mica increased at an even more rapid rate with thickness. In this connection very thin films of water and alcohol, two very absorptive bodies, were found to be quite fairly transmissive, as were also collodion films, especially when thin enough either to appear black or to show the first order colours by reflected light. The thin liquid films were measured between polished plates of silver chloride, while the collodion films were picked up by rings from the surface of water.*

* Proc. Roy. Inst., xxi. p. 787.

A great number of bodies were studied. Those solid at ordinary temperature were usually ground and polished to the requisite thickness. If not obtainable in pieces of sufficient size, the powdered or crystalline material was compressed hydraulically into suitable plates, sometimes with the addition of a trace of solvent. Fusible substances were usually cast. Mica laminae were stripped in the usual way; while glass fragments of sufficient size ($2\frac{1}{2}$ cm. disc) but thinner than micro-cover glasses were selected from large thin bulbs. The majority of observations were, however, made on materials liquid at the ordinary temperature, although solid when cooled in liquid air; and various devices became necessary to get suitable plates of these for immersion above the cell. Several could, by careful partial cooling, be rendered sufficiently viscous to give a coherent disc when poured on a quartz plate supported above a liquid air surface. By further gradational cooling the viscous disc could very often be solidified to a clear glass usually quite readily separable from the quartz plate. The large number of substances which give clear glasses when properly cooled to liquid air temperature is very extraordinary, a crystalline disc being almost exceptional.

Another simple method was to use a tambourine of a rubber membrane stretched on a light metal ring ($2\frac{1}{2}$ to 3 cm. diameter). This could be first carefully cooled, and the measured quantity of liquid (also previously cooled as low as was practicable) poured in and finally solidified by immersion. In some cases the rubber membrane could be stripped off under liquid air, leaving the thin solidified plate; but this is not necessary if the small absorption of the membrane is previously measured, and is very often not practicable, as, e.g., when cracks are formed during the cooling. Previous cooling of the membrane and liquid separately allows reactive or very solvent liquids to be readily handled without attack on the membrane or its support; but in many cases the tambourine was carefully cooled with the liquid already in. The tambourine was supported by a vertical wire bent to a springy horizontal ring, clamped above a cup of liquid air, which was steadily screwed up to cool the membrane. A deep quartz cup floating on the liquid air surface (but without much lateral freedom) was an advantage in some cases where more controlled and slower cooling was found necessary to give the best results.

Thus the ordinary condensable gases, such as ammonia, sulphurous acid, hydrochloric acid, etc., could usually be dripped from the end of a delivery tube just above the membrane tambourine, supported at the appropriate height above the liquid air. After the liquid had been solidified by further cooling, weighing of the tambourine on a scale pan in an open vessel immersed in liquid air presented no serious difficulties.* The thickness of the condensed material was

* Proc. Roy. Soc., A. lxxxix. p. 158.

therefore easily obtained. When necessary a correction was made for the quantity in the curved surface of contact between the liquid and the ring. Screens of approximately 0.1 mm. thickness were readily obtained by using a tambourine of silk-gauze chiffon instead of a rubber membrane. This was dipped into the liquid to be examined, and when lifted out retained a fairly uniform layer in the tiny spaces between the crossed silk threads. Separate measures of the proportionate obstruction of the stretched gauze alone showed that only 30 per cent. was stopped: a result found to be in agreement with microscopic measurements of the threads and spaces of the material. The wetted gauze was then cooled as rapidly as possible and weighed in the same way as the membranes, etc. The chief objection is that the mixed liquid and silk surfaces are not strictly plane.

The results obtained are grouped later, but some aspects of their interpretation should first be dealt with. An obvious correction to such measures is the reflection loss from the plane surfaces. This, as given by Fresnel, is $y = \left(\frac{n - 1}{n + 1} \right)^2$, where y is the proportion reflected at the surface, and n the index of refraction between the media separated by this surface.

The curve (Fig. 11) shows the growth of y (ordinate) with n the index of refraction (abscissa). The upper curve is for substances in air, and the lower curve gives the reduced values of y in liquid air for values of n , corrected by $\frac{1.0}{1.22}$, the relative indices for air, gaseous and liquid. Table III. gives the values for four typical substances with increasing n , corresponding to normally incident "D" line radiation.

TABLE III.

Substance	Ref. Index n	Per Cent. Reflected	
		Air	Liquid Air
Indiarubber	1.5	4.0	1.1
Silver chloride	2.06	12.0	6.4
Iodine	3.31	29.2	21.2
Stibnite	5.29	45.2	38.8

This correction for the rubber membrane or rock-salt is within the experimental error, but for silver chloride is quite considerable. When this substance is used to obtain very thin capillary films of different liquids, the results may be quite misleading unless carefully analysed. So also for direct measurements of iodine or other very refractive materials. This is, however, fairly simple on the

assumption of ordinary "D" light, but the actual radiation measured is very different from this, and the consequent correction to be applied is doubtful.

In this connection it is as well to recall the altering wave length of the region of maximum radiation as the temperature of the source is changed. This is illustrated by Figs. 15 and 16. The first set of

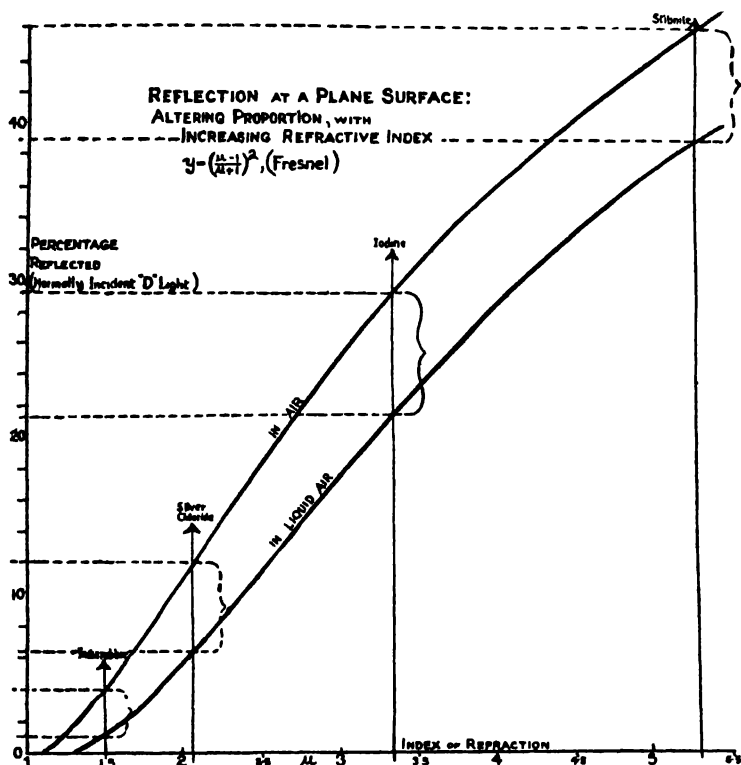


FIG. 14.

curves are from Lummer and Pringsheim's results. The second, at lower temperatures, are calculated from Planck's formula—

$$J_{\lambda} = \lambda^{-5} \times C_1 \left(e^{\frac{C_2}{\lambda T}} - 1 \right)^{-1}$$

(as given in the Smithsonian Physical Tables, 1920, p. 247).

At a temperature of 1650° Abs. the maximum theoretical wave length emitted is of the order 2μ , while by the time a source is

reached whose temperature is down to $-80^{\circ}\text{C}.$, the maximum has increased to a wave length of 16μ , and of course at lower tempera-

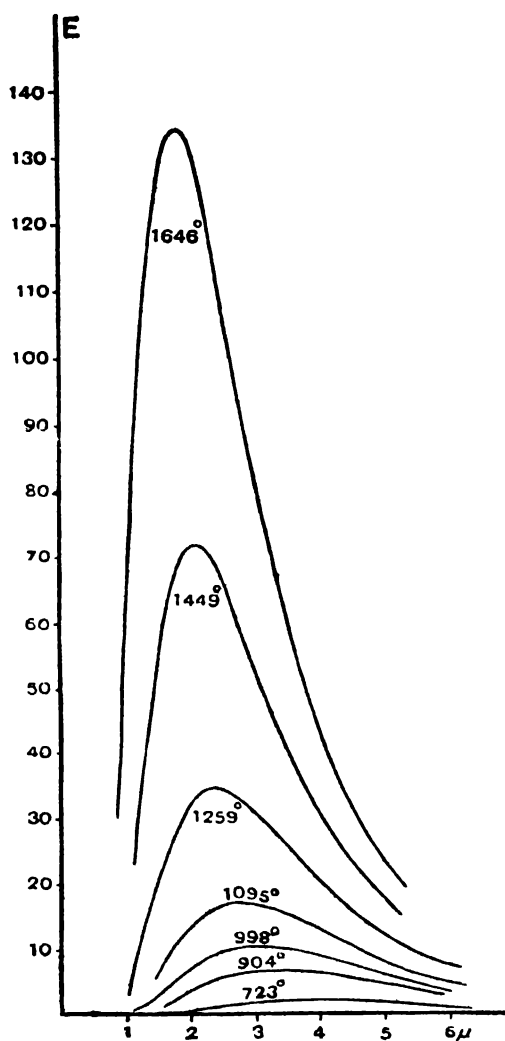


FIG. 15.

tures there would be even longer waves, a region scarcely yet explored with this thermoscope. Wien gives a simple relation

between wave length of maximum radiation intensity from black body and absolute temperature—viz. $\lambda T = 2930$, where λ is the wave length in microns (μ) and T is the absolute temperature. Some

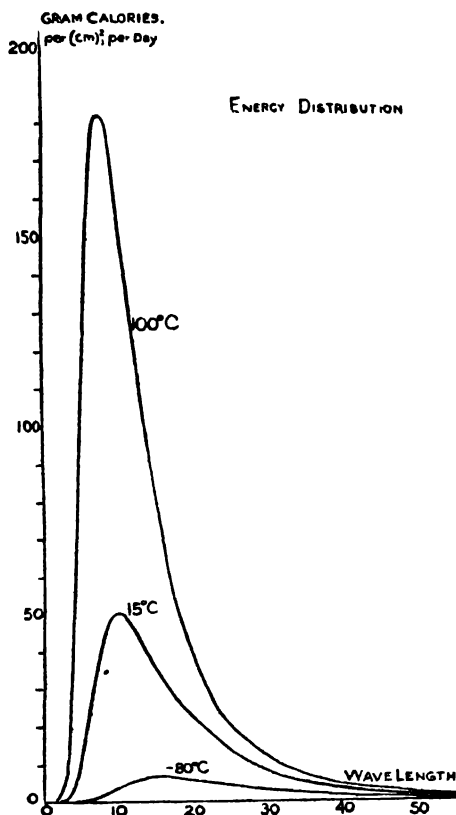


FIG 16.—HEAT SPECTRUM AT THREE DIFFERENT TEMPERATURES

typical temperatures and wave lengths calculated from this formula are given in Table IV.

TABLE IV

T . .	373	273	195	90	78	50	20	14	5	2
λ . .	8	11	15	32	38	58	146	209	566	1465

Rubens and Kurlbaum, on the other hand, experimenting with specially sifted radiations of wave length, $24\ \mu$ and $31.6\ \mu$, and using a black source down to liquid air temperatures, got results which do not agree with these values.

Assuming "D" line radiation, the following examples will illustrate the order of the corrections to be made. In the case of rock-salt there are only small variations of the index of refraction with rather large changes in wave length, as shown in Table V.

TABLE V.

Wave length (μ)	0.6 ("D")	8	11	16
Refractive index.	1.545	1.507	1.481	1.44
T° Abs.	—	373°	273°	183°

In this case, therefore, the error from taking the indices corresponding to the "D" line will not be very serious, a result which does not hold for silver chloride.

Taking the cases of films of water and alcohol respectively, between plates of silver chloride, the transmissions recorded were 18 per cent. for water and 58 per cent. for alcohol, the thickness of film being $0.088\ \text{mm.}$ for water and $0.040\ \text{mm.}$ for alcohol.

Now if for simplicity we take

$$R + A + T = 100 \text{ per cent.},$$

where R = the reflections. A = the absorptions, and T = the observed transmission, then of the reflections there will be two between silver chloride and liquid air surfaces, and two between silver chloride and ice surfaces. The calculated "Fresnel" reflection-corrections are 6.7 per cent. for the liquid air surfaces and 4.6 per cent. for the ice surfaces. The total reflection-corrections are therefore

$$2 \times 6.7 + 2 \times 4.6 = 22.6 \text{ per cent.}$$

The absorption of the silver chloride plates (separately measured and corrected for liquid air reflections) is only 1.2 per cent., so that each plate reduces the incident radiation by 11.9 per cent.

Thus 88.1 per cent. is transmitted by each plate. Since 18 per cent. emerges from the second plate, the proportion transmitted by the ice between the plates is

$$18 \left(\frac{100}{88.1} \right)^2 = 23.2 \text{ per cent.}$$

Similarly with the alcohol: assuming the same refractive index as for ice, the transmission by each plate is 88.1 per cent.: then since 54 per cent. emerges in this case, the proportion transmitted by the alcohol alone is

$$54 \left(\frac{100}{88.1} \right)^2 = 69.6 \text{ per cent.}$$

Several other liquids were similarly studied, such as methylene iodide and chinoline. (See Fig. 17.)

A chinoline film gave observed transmission of 54 per cent. With a refractive index at each silver chloride-chinoline surface of 1.268, the reflected proportion will be 1.4 per cent.; this with the 6.7 per cent. at each silver chloride-liquid air surface would result

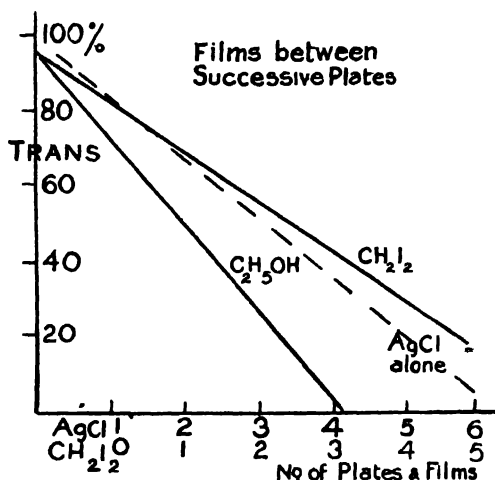


FIG. 17.

in a corrected transmission of 65 per cent. for the chinoline film alone. By the same method of taking a fractional diminution at successive surfaces, based on the refractive index through each surface, the transmissions were worked out for three films of alcohol and four films of methylene iodide, enclosed respectively by four and five silver chloride plates in succession. The transmissions were observed at each step as the piles of plates and solidified films were built up. The results are given in Fig. 17. The calculated transmissions through the successive alcohol films were 72.7 per cent., 65.2 per cent., and 65.1 per cent.; and through the methylene iodide films, 76.5 per cent., 79.1 per cent., 80.6 per cent., and 78.9 per cent. These values were deduced on a transmission factor of 0.9345 for

each silver chloride-alcohol surface, and 0.993 for each silver chloride-methylene iodide surface, applied to the observations obtained at each step.

Rock-salt with its lower refractive index would be preferable to silver chloride for such measurements, except that it has to be cooled so slowly to avoid cracking that much more time is required, whereas silver chloride in thin rolled plates is very easily handled. Two superposed membranes with liquid films between are also quite workable.

Successful trials were made with a hollowed-out flat capsule of rock-salt fitted with a plane cover plate when necessary. By this means plane layers of substances of definite thickness were obtained.

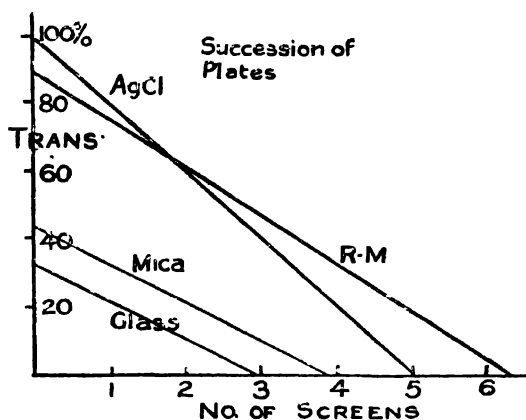


FIG. 18

With ordinary liquids the whole reflection correction is very small, being practically the same as for a rock-salt plate alone—namely, 2.7 per cent. in liquid air (for the “D” line). This cell was to be used for measuring the transmissive powers of liquid gases (such as methane) with a “gas-cooled” thermoscope. With liquid immersion in the ordinary way, the cover plate would be necessary. This, however, was not carried out.

The transmission through a succession of plates of silver chloride alone was also measured for the purpose of studying the rate of extinction of incident radiation by successive reflections. Thin membranes and thin discs of mica and glass were also measured. The results observed are shown in Fig. 18.

A simplified method for several surfaces has been pointed out

by Provostaye and Desains.* Thus, if there are m surfaces, and $y = \left(\frac{n-1}{n+1}\right)^2$ reflected at each surface, then for m surfaces $Y = \frac{m y}{1 + (m-1) y}$ will be reflected, and therefore $1 - Y = \frac{1 - y}{1 + (m-1) y}$ transmitted. This expression applied to (1) rock-salt, (2) silver chloride, and (3) iodine, gives the values shown in Table VI.

TABLE VI.

(1) <i>Rock-salt</i> (or glass, mica, rubber membrane, approximately).				<i>In liquid air, n=1.266, y=0.0136.</i>		
<i>In air, n = 1.544, y = 0.0456.</i>						
Plates	Surfaces	Y	1 - Y		Y	1 - Y
		per cent	per cent		per cent.	per cent
1	2	8.7	91.3		2.68	97.32
2	4	16.04	83.96		5.23	94.77
3	6	22.3	77.7		7.64	92.36
(2) <i>Silver chloride.</i>				<i>In liquid air, n=1.69, y=0.0658</i>		
<i>In air, n = 2.06, y = 0.12.</i>						
1	2	21.4	78.6		12.3	87.7
2	4	35.3	64.7		22.0	78.0
3	6	45.0	55.0		29.7	70.3
(3) <i>Iodine.</i>				<i>In liquid air, n=2.738, y=0.2162.</i>		
<i>In air, n = 3.34, y = 0.2907.</i>						
1	2	45.04	54.96		35.6	64.4
2	4	62.12	37.88		52.5	47.5
3	6	71.1	28.9		62.3	37.7

In the case of both silver chloride and rubber membranes, as shown by Fig. 18, the observed values diminished more rapidly than these tables indicate. Thus three silver chloride plates only transmitted 49 per cent. observed as against 70.3 per cent. if there were only reflection losses. When all account is taken of the indi-

* Ann de Chim, xxx. p. 159, 1850.

vidual absorptions, there still appears some discrepancy, so that probably the index of refraction employed (that for "D" light) is not sufficiently near for the dark radiation employed, especially with a substance of such relatively high index as silver chloride. The observed values may, however, be utilised in a reverse calculation to that given above—i.e. to determine the effective index of refraction to give the observed reflection losses. Using the observed $Y = 0.51$ (49 per cent. transmitted) and $m = 6$, then $y = 0.148$, whence $n = 2.25$, instead of the 1.69 employed in the previous table.

TABULATED VALUES OF TRANSMISSIVE POWER.

Owing to the great heat-absorptive power of water, the principal precaution to be taken in preparing substances for these observations is to ensure perfect dehydration.

Among the more simple bodies carbon disulphide and iodine are well known as very perfect transmitters of heat at ordinary temperatures, and they preserve this property at low temperatures. Tetrachloride of carbon and thiophosgene are similarly very transmissive. Phosphorus is remarkable, for while its observed transmission is 76 per cent, when this is corrected for reflections less than 10 per cent. remains to represent the maximum absorption, which is thus even less than that of iodine, and of the same order as rock-salt and the chloride and bromide of silver.

The paraffins and benzene exhibit high transmissive powers, and halogen substitution generally increases the value. Alcohols, ketones, acids and similar bodies are absorptive, as also are amides, nitro-bodies, etc. Esters are generally more transmissive, while pyridine and its associates are still better.

The principal results are grouped in the following tables. There are four columns in addition to the one describing the substance. Of these the first indicates the condition of the cooled substance: G being for a glass and C for a crystalline structure. The support or means of securing the disc is shown in the second column; RM indicates that the material was solidified in a rubber-membrane tambourine, Ch that the chiffon gauze was employed as already described, and P that the material was in the form of a plate compressed or frozen. The thickness in mm. is given in the third column, and the observed per cent. transmission in the fourth.

Substance	1	2	3	4
<i>Simple Compounds, etc.</i>				
Sulphuric acid	G	P	0·6	2·5
Hydrochloric acid	G	RM	0·5	11
Sulphurous acid	O	"	"	20
Ammonia	C	"	2·0	4
Phosphorus *	—	P	0·75	90
Iodine *	—	"	0·8	80
Bromine	G	"	0·5	10
Carbon tetrachloride	O	RM	"	56
Thiophosgene	G	Ch	0·1	53
Carbon disulphide	G	RM	0·5	70
Mercaptan	G	RM	0·5	21
Sodium	—	—	1·0	4
Selenite	—	—	0·1	8
Chrome alum	—	—	1·0	6
	—	—	3·0	4

* Corrected for reflection.

<i>Common Substances</i>				
Glass	—	—	0·25	14
	—	—	0·125	19
	—	—	0·012	37
	—	—	0·006	40
Mica, white	—	—	0·1	5
	—	—	0·063	8
	—	—	0·025	24
	—	—	0·013	33
" black	—	—	0·17	10
	—	—	0·06	13
	—	—	0·023	26
	—	—	0·013	33
Celluloid	—	—	0·125	7
Collodion films	—	—	Blue†	86
	—	—	Amber†	90
	—	—	Black†	94
Gelatin	—	—	0·02	35
" 2 discs	—	—	2× "	15
" 3 "	—	—	3× "	10
Goldbeater's skin	—	—	—	15
Ebonite	—	—	0·5	13
India-rubber	—	—	0·625	4
	—	—	0·25	9
	—	—	0·1	30
	—	—	0·05	55
	—	—	0·02	80

† By reflected light.

Substance	1	2	3	4
<i>Hydrocarbons (Aliphatic)</i>				
Pentane (n. or i)	G	RM	0·5	58
„ iso-propyl ethane	G	RM	0·5	74
„ „ „ „ „ „ „ „ „ „	„	Ch	0·1	77
Hexane n.	„	RM	0·5	47
„ „ „ „ „ „ „ „ „ „	C	Ch	0·1	55
Heptane	G	RM	0·5	51
Octane	G	RM	0·5	60
„ „ „ „ „ „ „ „ „ „	G	RM	3·1	32
Decane (di-iso-amyl)	G	„	0·5	52
„ „ „ „ „ „ „ „ „ „	G	Ch	0·1	78
Amylene	G	RM	0·5	15
Diallyl	G	RM	0·5	21
Dipropargyl	G	RM	0·5	11
Isoprene	G	Ch	0·1	40
β γ Dimethyl butadiene	G	Ch	0·1	74

<i>Hydrocarbons (Aromatic)</i>				
Benzene	G	RM	0·5	49
„ „ „ „ „ „ „ „ „ „	„	Ch	0·1	55
(Dipropargyl	„	RM	0·5	11)
Toluene	„	„	„	34
Ethyl-benzene	„	„	„	28
Propyl- „	„	„	„	27
Xylene	„	„	„	25
„ „ „ „ „ „ „ „ „ „	„	„	„	38
Cyclo-hexane	„	Ch	0·1	53
(Cyclo-hexanol	„	RM	0·5	19)
(Cyclo-hexanone	„	„	„	20)
Naphthalene	C	P	1·3	19

<i>Halogen substituted bodies</i>				
Methyl iodide	G	RM	0·5	40
Ethyl chloride	„	„	„	36
„ bromide	„	„	„	40
„ iodide	„	„	„	53
Propyl iodide (n.)	„	„	„	24
Allyl „	„	„	„	44
Hexyl „	„	„	„	28
„ „ „ „ „ „ „ „ „ „	C	„	„	43
Chloroform	C	Ch	0·1	58
Methylene chloride	G	RM	0·5	51
„ iodide	„	„	„	45
Ethylidene chloride	„	„	„	40
Acetylene tetrachloride	„	„	„	58

Substance	1	2	3	4
<i>Halogen substituted bodies (cont.)</i>				
Chlor-benzene	G	RM	0.5	39
Di- " "	"	P	1.6	59
Per- " "	—	P	1.0	10
Benzene hexachloride	—	P	1.0	13
Brom-benzene	G	RM	0.5	31
Iodo- " "	C	"	"	24
Pyridine dichloride	"	P	"	37
" tetra "	"	RM	"	35
" penta "	"	"	"	40
α Chlor-naphthalene	G	"	"	42
α Brom- " "	"	"	"	42
(Glycerol	"	"	"	5)
Mono-chlor-hydrin	"	"	"	9
Di- " "	"	"	"	13
Tri- " "	"	"	"	17
Epi- " "	"	"	"	7

<i>Alcohols, Aldehydes, Ketones and Ethers</i>				
Methyl alcohol	G	RM	0.5	18
	"	Ch	0.1	27
	"	P	1.5	8
Ethyl alcohol	"	RM	0.5	17
	"	Ch	0.1	38
	"	—	0.04	70
Propyl alcohol	"	RM	0.5	20
	"	Ch	0.1	22
Propyl alcohol, iso	"	RM	0.5	15
Butyl alcohol n.	"	RM	0.5	33
" " tertiary	"	Ch	0.1	57
Amyl alcohol " "	"	RM	0.5	36
	"	Ch	0.1	41
Ethylene alcohol	"	RM	0.5	10
Propylene " "	"	"	"	8
Allyl " "	"	"	"	20
Paraldehyde	C	"	2.1	27
	C	"	0.5	38
Chloral	G	"	"	25
Propylaldehyde	"	"	"	8
Acetone	C	"	"	25
Methyl-ethyl-ketone	C	"	"	19
	G	"	1.5	37
Ether	"	"	0.5	41
	"	Ch	0.1	46
Glycerol	"	RM	0.5	5
Phenol	C	Ch	0.1	32
Benzaldehyde	G	RM	0.5	28
(Benzoic acid	—	P	1.7	9)
Salicylaldehyde	C	RM	0.5	10.5
Acetophenone	C	"	"	16

Substance	1	2	3	4
<i>Acids and Anhydrides, etc.</i>				
Formic acid	C	RM	0.5	8
Acetic "	G	"	"	7
Monochloroacetic acid	G	"	"	10
Di- " " " " " " " " " " " "	"	"	"	16
Tri- " " " " " " " " " " " "	"	"	"	19
Propionic acid	C	"	"	5
Valeric acid (sec)	G	"	"	2.5
Butyric " n.	G	"	"	4
(a Br " " " " " " " " " " " "	"	"	"	5)
Stearic " " " " " " " " " " " "	C	"	"	21
Oleic " " " " " " " " " " " "	G	Ch	0.1	24
Acetic anhydride	G	RM	0.5	20
Acetyl chloride	G	"	"	20

<i>Esters</i>				
Methyl acetat.	C	RM	0.5	25
Ethyl formate	G	"	"	16
" acetate	"	Ch	0.25	20
" chlor acetate	"	RM	0.1	46
Aceto-acetic ether	"	"	0.5	28
Ethylene acetate	"	"	"	5
Amyl " " " " " " " " " " " "	"	"	"	15
Methyl oxalate	C	"	"	14
Ethyl " " " " " " " " " " " "	"	Ch	0.1	8
Ethyl carbonate	"	RM	0.5	20
Ethyl ester of eth. malonic acid	G	"	"	15
" " " me. " " " " " " " "	C	"	"	8
Methyl " " malonic acid	G	"	"	27
Glycol bi-acetate	"	"	"	4
Triacetin	"	"	"	25

<i>Amines, Amides, etc.</i>				
Trimethylamine... ..	G	RM	0.5	13
Triethylamine	"	"	"	24
Amylamine	"	"	"	10
Formamide	C	"	"	11
Acetamide	G	"	"	27
Urea	G	Ch	0.1	11
Aniline	G	RM	1.4	21
Diethyl aniline	"	"	0.5	28
Dimethyl " " " " " " " " " " " "	C	"	"	28
Toluidene o.	G	"	"	11
Xylidene 1 : 3 : 4	"	"	"	14
Phenylhydrazine	"	"	"	2

Substance	1	2	3	4
<i>Amines, amides, etc. (cont)</i>				
NH ₄ I	—	P	0.7	16
N(CH ₃) ₃ I	—	"	1.5	43
N(C ₂ H ₅) ₄ I	—	"	1.1	22
<i>Cyanides, Nitriles, Nitro-bodies, etc.</i>				
Cyanogen... ..	G	RM	0.5	30
Aceto-nitrile	C	"	"	28
Proprio- "	"	"	"	18
Valero- " (iso)	G	"	"	19
Butyro- "	"	"	"	15
Ethyl cyanoacetate	"	"	"	8
Amyl nitrite	"	"	"	6½
Nitromethane	G	"	"	35
Benzyl cyanide	G	"	"	12
Benzonitrile	C	"	"	19
Nitrobenzene	C	"	"	21
" toluene	C	"	"	10
<i>Pyridine and allied bodies</i>				
Pyridine	G	RM	0.5	42
Picoline	"	"	"	53
Lutidine	"	"	"	35
Chinoline... ..	"	P	0.7	30
Pyrrol	"	Ch	0.1	28
Nicotine	"	RM	0.5	10
(Thiophene	"	"	"	28)
(Furfural	"	"	"	18)
<i>Tri-azo bodies</i>				
Tri-azo benzene	G	RM	0.5	24
" ethanol	"	"	"	2½
" acetic ester	"	"	"	16
" ethyl acetate	"	"	"	8
Ethyl tri-azo acetate	"	"	"	6
" " propionate	"	"	"	13
<i>Turpentine</i>				
Turpentine	G	RM	1.0	2
Camphor	"	P	0.5	5
Monobrom-camphor	—	"	1.3	10
α Dibrom- "	—	"	1.5	21
			1.3	6

Several normally absorptive substances when sufficiently reduced in thickness were found to behave like india-rubber and permit a considerable transmission. The curves of Fig. 19 give some instances

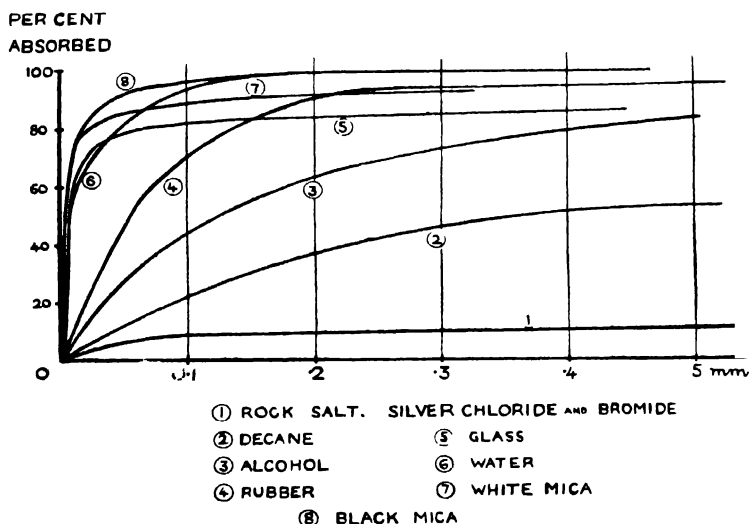


FIG 19

In the case of bodies crystalline at low temperatures some of the heat will be diffused. To estimate the possible error thus involved several preparations were made of rock-salt, graded from polished transparent plates to opaque blocks. The resulting values are shown in the next table.

ROCK-SALT TRANSMISSIONS.

Rock-Salt, 1 mm thick	Heat Transmission
Plate, 2 polished surfaces	90% to 94%
" 1 " and 1 rough surface	72% to 76%
" 2 roughened surfaces	62% to 64%
Ground finely and compressed .	70%
Ditto ditto after brine moistening	31%
NaCl precipitated by alcohol; dried and compressed }	50%
Ditto ditto, after brine moistening ...	18%

The comparison between polished rolled silver chloride and bromide and a compressed plate of silver iodide is also interesting,

and is given in the following table (without any correction for reflection):—

Plate	Thickness	Transmitted proportion
Silver chloride	0·15 to 1 mm.	84% to 85%
Silver bromide	0·5 to 1 mm.	83% to 86%
Silver iodide... ..	1·2 mm.	65%

A certain number of observations were made with the black body source cooled by boiling solid carbonic acid. The values obtained were not very different from those already given. The following table gives comparative results for a few typical bodies :—

Substance	Temperature of Source			
	-78° C	11° C	100° C	
Rock salt	91	94	94	Transmission
Silver chloride	82	80	80	
Rubber membrane	78	76	75	
Mica (0·025 mm.)	33	30	28	
Glass (0·125 mm)	21	20	19	

Observations of the emissivity of various substances, as polished plates, placed above the thermoscope gave the following values in comparison with the black Leslie cube :—

EMISSIONS AT 100° C.

Thermoscope Observations.

"Black Body"	100
Iron	14
Lead	14
Tin	12
Aluminium	9
Zinc	7
Nickel Silver	6
Pewter	5
Copper	5
Brass	5
Mercury	3

Acknowledgment is due to Mr. W. J. Green, B.Sc., for the valuable assistance he rendered during the progress of the work and in the preparation of this abstract.

[J. D.]

Friday, January 23, 1920.

GENERAL E. H. HILLS, C.M.G. D.Sc. F.R.S., Secretary and
Vice-President, in the Chair.

THE HON. SIR CHARLES PARSONS, K.C.B. Sc.D.
LL.D. F.R.S. M.R.I.

Researches at High Pressures and Temperatures.

THE subject to which I wish to direct our attention this evening is Researches at High Temperatures and Pressures.

Just ten years ago, in this room, Sir Richard Threlfall discussed the effects of temperature and pressure on various substances, and commenced by referring to a suggestion I made in 1904 to sink a bore hole 12 miles deep in the earth with the object of exploring the region beneath us, about which so little is known. Last summer, at Bournemouth, I ventured again to direct attention to the desirability of such an exploration in the interests of science generally, and to the possibility that it might ultimately lead to some developments of practical importance and utility.

Ten years ago no experiments had been made on the behaviour of rocks under the conditions existing at great depths below the surface of the ground; but prompted by my suggestion in 1904, and some subsequent correspondence in regard to the possibility of the rock crushing in and closing the shaft, Professor Frank D. Adams, of McGill University, Montreal, commenced experiments on the strength of rocks to resist the closing up of cavities under the conditions prevailing at great depths below the surface. He published the account of these experiments in 1912, in the *Journal of Geology* for February of that year.

Adams' method was to place a block of granite or limestone in a tightly fitting cylinder of nickel steel which was shrunk lightly around the block to ensure perfect fitting and support; hard steel rams actuated by a hydraulic press were arranged to press against the ends of the block with a known pressure. Two small holes were previously drilled in the specimen, one axial in the centre and one transverse, the diameter of the holes being 0.05 inch, or one-tenth the diameter of the specimen. The temperature of the container and specimen were maintained at any desired point up to the softening point of steel. In some experiments no heat was applied, in others

the temperature was raised to that estimated to exist at the depth below the surface of the earth corresponding to this pressure.

When no heat was applied the holes in the granite showed no alteration under a pressure equivalent to 30 miles deep, and in the case of limestone the specimen supported one-half of this pressure without alteration. He then raised the temperature of the container and specimen. When granite was heated to 550°C ., a temperature corresponding to 11 miles below the surface, it stood a pressure equivalent to 15 miles, and might have stood more but that the container became weakened by the heat. Limestone begins to decompose at a temperature of 450°C ., but even at this temperature it withstood a pressure corresponding to 10 miles.

Adams concludes that small cavities in granite will not close in under the conditions of pressure and temperature at 11 miles below the surface, however long a time is allowed to lapse, and that the cavities may persist to much greater depths; but the softening of the steel of the container precluded the carrying of his experiments to still higher temperatures and pressures.

As far as they go these experiments are reassuring as to the permanence and safety of a pit shaft 12 miles deep sunk through granite. But it would be more satisfactory to experiment on a larger specimen than one only $\frac{1}{2}$ inch in diameter, as used by Adams, and to electrically heat the specimen when submerged in graphite while keeping the container cold, the temperature being indicated by a thermo-couple in the specimen; this could be carried out in a nickel steel container like Fig. 5.

In this connect on P. W. Bridgeman in 1911 submerged a sealed glass tube containing a cavity under an external hydrostatic pressure of 24,000 atmospheres (corresponding to a depth in the earth of 56 miles) for three hours, and the cavity showed no change in size or form. It, however, appears that temperature will probably place a limit to the depth that would be reached before closing in of the shaft commences to occur, for Judd, Milne and Mallet agree in the view that the deepest origin of earthquakes is between 30 and 50 miles. This would seem to indicate that at greater depths than 30 miles the temperature and pressure are such that changes of form take place by plastic deformation, and not by sudden slips or the formation of faults, which are the chief cause of earthquakes. Again, Oldham states that beyond 20 miles deep seismic waves which are transmitted by compression and distortional vibrations change in character in this respect: that though the compressional waves are only slightly affected in velocity, on the other hand the distortional waves are reduced to one-half their velocity. This would seem to imply that the modulus of elasticity in shear has, at 20 miles depth, fallen to one-half owing to the rise of temperature, and it seems probable that the rock also is weakening in its resistance to shear: in

fact that the rock is becoming more plastic, and that cavities would probably close up at 20 miles below the surface.

The deepest single stage shaft on the Rand is Hercules E.R. P.M. It is 4500 feet vertically and is rectangular in section.

The deepest shaft in the world is Morre Velho. The bottom is 6400 feet vertically below the surface, and it has been sunk, and is worked in stages, two of which are about 1200 feet vertical. The deepest shaft designed on the Rand is by the City Deep Company. It is 7000 feet vertically, is circular of 20 feet diameter, and is to be worked in two stages of 3500 feet each.

The most rapid sinking record was made at the Crown Mines No. 15 Shaft, where 310 feet were sunk in a month. It is circular and of 20 feet in diameter. There are several interesting departures from ordinary mining practice necessary even at this depth. The haulage is arranged in stages of about half a mile, principally in order to economise the weight of rope, and also the power for winding. In countries where the atmosphere is dry the sides of the shaft are cooled by sprinkling water upon them, which by evaporation cools the rock. It is however possible to augment this effect by artificially drying and cooling the air before passing it down the mine.

When still greater depths of shaft are in contemplation, further methods of cooling in addition to these would probably be found necessary—for instance, the carrying the heat upwards by means of brine circulated in a closed ring formed of steel pipes with a rising and descending column. Though the columns might be carried the whole depth of 12 miles, the hydraulic pressure at the bottom would be about 12 tons per square inch, and would entail very costly pipes of great strength to resist the pressure. A cheaper plan would be to work in stages, each ring occupying a stage of from 2 to 3 miles of the shaft, the heat being transferred from the top of one brine ring to the bottom of the ring above by surface heat exchangers and refrigerating machinery to neutralise the heat drop on transfer; these may be called heat pumps and would be driven electrically.

As the depth of the shaft increases the pressure of the air upon the miners will be about doubled for every 2 to 3 miles, but what is more serious is the increase of temperature of the air itself caused by the adiabatic compression due to gravity, by which it will be raised about 100° F. For these reasons it will be necessary to place air-tight partitions across the shaft at every mile or two, and to carry on the ventilation through these by means of a pump to deliver the foul air upwards, and an expander to allow the fresh air to descend; these two machines would be linked together and the difference in their power supplied by an electric motor (this method has been often used with water and is equally applicable to air). At each partition heat exchangers and refrigerating machinery similar to that used for the brine would be placed.

When sinking the deeper portions of the shaft probably shields would be necessary to protect the miners from the splinting of the rock which is caused by the intense compressive stress which splits off scales from the surface, sometimes with considerable violence.

In 1904 the estimate of the time required to sink 12 miles was eighty years and was based on the records at that time. With improved machinery and methods the records have been so much lowered (at the Crown mines 310 feet of a circular 20 feet dia-shaft have been sunk in a month) that an estimate of thirty years seems now to be reasonable.

Threlfall traced the gradual evolution of the theory of the effects of temperature and pressure on the allotropic forms of various substances, their critical temperatures and conditions of gaseous, liquid and fluid states. He described his apparatus and experiments designed to melt graphite under high pressure, his inference being, that under pressures up to 100 tons per square inch carbon does not follow the same law as many other substances, and does not crystallize as diamond on cooling.

An interesting discovery was made by Bridgeman in 1911 when studying the compressibility of mercury. He found that it had a remarkable power of penetrating steel containers, more especially those made of hardened and tempered steel; a power not possessed by oil or water, and which caused them to burst at much lower pressures than when they were charged with oil or water. The phenomenon he attributed to the fact that mercury has the power of dissolving small percentages of iron, and will amalgamate with it when the surfaces are absolutely free from oxide.

In 1912 Bridgeman published his remarkable researches on water under pressures up to 20,000 atmospheres. He found that there are four allotropic forms of ice besides ordinary ice, which are found under various conditions of pressure and temperature with determinate regions of stability. All these forms, except ordinary ice, are more dense than water. One of these forms is remarkable as existing from a temperature of -18° C. under a pressure of 4500 atmospheres up to a temperature of 67° C. under a pressure of 20,000 atmospheres.

Recently a pressure of from 200 to 1000 atmospheres at a temperature between 500° and 700° C. has been applied to compel hydrogen to combine with nitrogen to form ammonia on a great commercial scale; a catalyst being necessary to promote the combination and to establish the equilibrium between the gases and their product. This action is reversible as regards temperature and pressure. On the other hand, iron just molten is an energetic catalyst in the transformation of diamond into graphite, but contrary to expectations, as we shall see, no amount of pressure that has as yet been applied appears to have caused a reversal of this action.

More than thirty years ago, having suitable apparatus at hand, I made a few experiments to try the effect of high pressures and

temperatures on carbon, compounds of carbon and some other substances.

The apparatus consisted of an 80-ton press under which suitable containers were placed, and a turbo-generator of 24 kilowatts output at 80 volts provided the current. It had been discovered by Cheesborough that the carbon filaments for incandescent lamps became very hard and resilient when heated in a hydrocarbon atmosphere of about $\frac{1}{2}$ H₂ absolute pressure, and I was anxious to try what would be the result if a rod of carbon were electrically heated when submerged in a liquid hydrocarbon under high pressure. Benzine, paraffin, treacle, chloride and bisulphide of carbon were tested under a pressure of 2200 atmospheres, or about 15 tons per sq. inch. The results were not successful in producing a hard coating to the rod, or of increasing materially its density and hardness, except in the case of tetrachloride of carbon, which slightly consolidated and hardened it; on the contrary, the carbon deposited from the liquids always appeared as soft amorphous carbon like soot. These experiments were extended by substituting instead of the liquids mentioned, silica, alumina and other substances, and increasing the pressure to 30 tons per square inch. When the current density was sufficiently increased the rod was converted to soft graphite. Moissan, in 1903, expressed the view that iron in a pasty condition was the matrix of the diamond, and that great pressure was the determining factor, which compelled a minute fraction of the carbon present to appear as diamond. He further speaks of the probability of carbon being liquefied when under a pressure sufficient to prevent its volatilisation, and that from the liquid state it may pass into the crystalline form on cooling. Crookes, in his lecture delivered before the British Association at Kimberley in 1905, emphasized the same view as to the probability of the crystallization of carbon directly from the molten state on cooling.

Though my original experiments in 1888 were not favourable to these views, it seemed however desirable to carry the investigations up to the greatest possible pressures attainable. Experiments were consequently resumed in 1907 with a new equipment, which consisted of a 2000 ton hydraulic press and a storage battery of 360 kilowatts output. The battery can be coupled for 2, 4, 8, 16, 48 volt as required, and the mains and the main switch can carry currents up to 80,000 amperes to the hydraulic press, which is placed by itself in a small strong house, partly below ground, with walls of 2 feet thickness reinforced with steel bars; the door is of 3 inches thick, the roof is of light galvanised iron. The container under the press is further enclosed by 2 inch thick telescoping steel rings, raised into position by steel ropes and counterweights. These precautions, as experience showed, were necessary, as several violent explosions occurred which cracked the steel rings and blew off the roof. A charge of iron and carbon when confined and raised to

a high temperature may be very violent if suddenly released by the melting of the pole pieces; also some endothermic compounds have been formed which swelled the container and allowed the contents to escape.

My experiments confirmed the conclusion at which Threlfall had independently arrived, that under pressures up to 100 tons per square inch, and very intense heating by electrical current, graphite is not materially changed. But modifications in the experiments were made, and other methods adopted, as will be explained, which in some respects carried the investigation to still higher pressures and temperatures; these however lead to the same conclusion.

This evening I propose to deal to some extent with the practical or engineering side of the subject, and to review the limits of pressure and temperature which are artificially attainable, and to make some comparison between them and the pressures and temperatures occurring in nature.

When the blade of a knife is pressed strongly against another blade so as to make a dent in each, the pressure on the boundary surface of the metal at the notch will have averaged from 300 to 350 tons per square inch, according to the hardness of temper of the steel. The pressures on the knife edges of a weighing machine when fully loaded are also of the same order.

When a needle is broken, or a piece of piano wire is strained to the point of breaking, the maximum tension on the metal will be at the rate of 150 tons per square inch.

On the other hand, the pressures that occur in the chambers of large guns do not usually exceed 20 tons per square inch, and the tensile stress on the plates of a ship in heavy weather should not exceed 8 tons per square inch.

From these simple instances some idea is gathered of the limitations imposed by materials and dimensions upon apparatus for experimenting at high pressures because of the practical difficulty of hardening and tempering steel in large masses.

When dealing with small amounts of material in each experiment the dimensions allow of the container and the ram being made of tungsten steel, which is a material that can be hardened and tempered throughout, and not only superficially as in the case of ordinary carbon steel. The material is hard and strong, but not brittle, and it retains these qualities up to moderate temperatures, such as 600° C., to a much greater extent than any other steel. Fig. 1 shows a container or die the bore is $1\frac{1}{2}$ inches in diameter, and it may be used for a limited number of times for a pressure of 200 tons per square inch. It will however eventually crack if this pressure is many times repeated, the cracks usually beginning near the bottom of the die.

For still higher pressures it is better to use a double re-entrant container (Fig. 2), with two rams, $\frac{1}{2}$ inch in diameter; both the container and the rams are made of hardened and tempered tungsten steel,

and are made fluid and gas tight by mild steel cups on the ends of the rams.

If the charge occupies only a short length of the bore as shown, the barrel of the container where the charge lies is supported by the sheer strength of the metal above and below the zone of pressure, in addition to its own strength as a tube; under these conditions it is as strong or stronger than the crushing strength of the rams, and pressures of 300 tons per square inch may be repeated several times without cracking.

In a container of this form 7 grains of fulminate of mercury have been placed, imbedded in graphite, and the pressure increased very gradually till it reached 230 tons per square inch (under this treatment fulminate does not usually detonate); the die was then heated by gas to over 180°C ., the temperature of detonation. After two failures of the experiment, owing to the leakage of the steel cups, the third was successful and no gas escaped, and the container was uninjured.

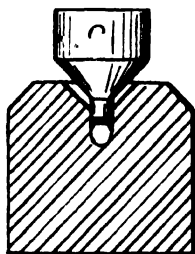


FIG. 1.

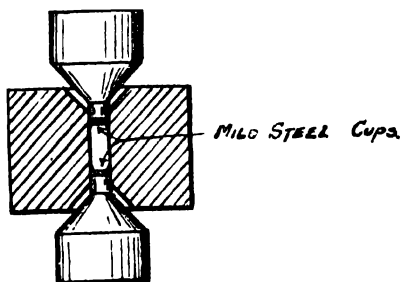


FIG. 2.

The graphite was somewhat caked, but otherwise unaltered. Graphite mixed with sodium nitrate and fulminate was also exploded under the same conditions.

Graphite with 15 per cent. of potassium chloride detonated when 200 tons per square inch had been reached.

Many other reactions were tested in a similar manner in larger dies under pressures of from 40 to 200 tons. The action of concentrated sulphuric acid on sugar was accelerated by a pressure of 50 tons; but on the whole these experiments in dies failed to produce any interesting results.

Unfortunately, the heating of the die with its charge cannot be carried much above 500°C . without seriously weakening the strength of the steel and compelling a reduction of pressure. The electrical heating of the charge in such small dies while keeping the die cool presents great difficulties in electrical insulation on so small a scale to withstand such intense pressure, but I think that it might be accomplished in certain instances.

It has been suggested with the object of reaching higher pressures that a small die might be bodily immersed in a large container; doubtless it could be arranged, but it would be very cumbersome to work with, and would only add about 100 tons per square inch to the maximum pressure.

A better plan would be to follow the principle of the usual capped armour-piercing projectile, and to reinforce the rams and ends of the container by tightly fitting copper or bronze rings around the necks of the rams, keeping the parallel part of the noses as short as possible (Fig. 3).

When in operation the copper rings will be flattened and squeezed against the necks and shoulders of the rams, and also against the ends of the container, and by this means the parts that ordinarily would have to bear the maximum stress will have part of this stress transferred to other parts not so heavily stressed, and consequently

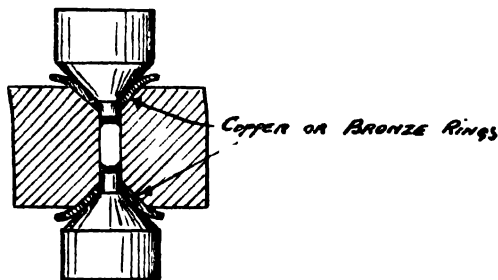


FIG. 3.

the maximum pressure in the container can by this means be raised considerably, perhaps to 450 tons per square inch.

In carrying out experiments on larger samples of material, and in applying electrical heating to the charge, the container becomes too large to permit of its being made of hardened steel; therefore nickel steel is used, as for the barrels of guns. It is heat-treated by quenching in oil from a high temperature after rough machining. Containers (Figs. 4 and 5) with the thickness of wall equal to the diameter of the bore will stand an internal pressure of 40 tons per square inch repeated almost indefinitely without serious enlargement of the bore; but 100 tons necessitates reborings and the fitting of new packing to the ram after each experiment.

Fig. 4 shows the arrangement for electrically heating conductors immersed in fluids under high pressure. The packing of the ram is a cup, leather, backed by a cup of brass; the leather first takes the pressure and the lip of the brass cup is thereby expanded tightly against the bore of the container and remains fluid-tight, even though the leather should be carbonized by the heat. The bottom

pole is electrically insulated from the container by vulcanized fibre washers and a rubber cup ring, which is protected from the heat by magnesite stemming.

The current is conveyed from the container to the top pole piece of the conductor by pads of copper gauze which can slide easily against the bore of the container and allow for the expansion of the conductor. Experiments on liquids with this container under 4400 atmospheres gave the same results as my former experiments under 2200 atmospheres.

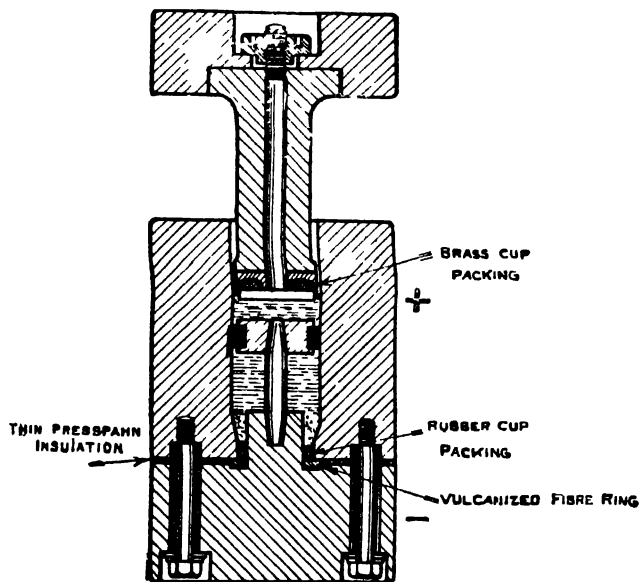


FIG. 4.

Fig. 5 shows the container arranged to melt graphite under pressure by resistance heating. Here the charge is graphite, and is divided by the bridge or ring made of pressed calcined magnesite or of titanium oxide. The bore of the container is electrically insulated from the graphite by layers of asbestos millboard and mica.

The calories evolved in the combination of graphite and oxygen are about half of 1 per cent. less than those evolved in the combination of diamond and oxygen, indicating that graphite at ordinary temperature is to this extent the stable state. The bulk pressure which has operated in some of the experiments would, however, seem to have been amply sufficient to turn the balance in favour of diamond instead of graphite. The uncertainty, on the other hand, as to the compressibilities and specific heats of the allotropic forms of carbon

under high pressures and at high temperatures renders speculation of little value as to what may occur at the melting point of carbon. All we know is, that up to the pressures and temperatures reached in our experiments no indication of a change from graphite to diamond has been produced. In one experiment very intense heating was applied for five seconds, but sufficient in amount to melt the graphite core six times over, the only result being a slight alteration of the structure of the graphite; the barrier in this experiment was calcined magnesia, and the hole in it was superficially converted to magnesium carbide. It appeared, however, desirable further to investigate the possibility of carbon losing its electrical conductivity when approach-

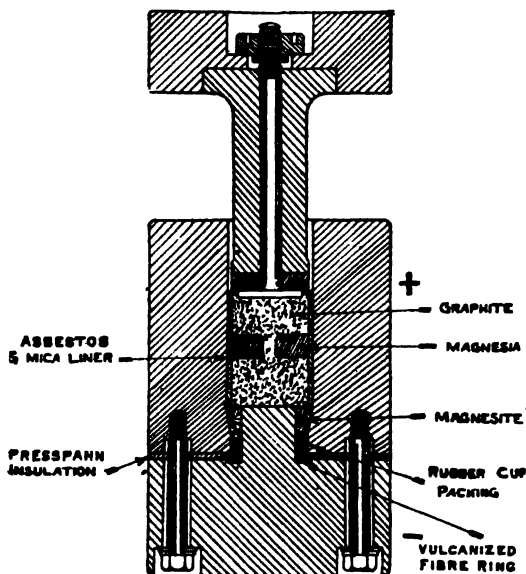


FIG. 5.

ing its melting point, as alleged by Ludwig and others, and of shunting the current from itself on to the contiguous molten layers of the insulating barriers surrounding it. There had been no indication of such a change having occurred, even momentarily; it rather seemed that the graphite core had been partially vaporized and condensed in the cooler parts of the charge. The experiment was repeated with rods of iron and tungsten embedded in the core, so that should the temperature of volatilization of the metals under a pressure of 15,000 atmospheres exceed that necessary to liquefy carbon under the same pressure, the presence of these metals might produce a different result. No change however occurred.

Note.—The temperature at which carbon, iron or tungsten volatilizes under a pressure of 15,000 atmospheres are unknown, but they are probably much higher than at atmospheric pressure.

This experiment also tested iron as a solvent of carbon, and as a catalyst from diamond to graphite under a pressure of 100 tons, and showed that under this pressure that action was not reversed.

Fig. 6 shows the container arranged for treating powders by resistance heating with or without the addition of liquids or gases.

The electric current is conveyed from the container to the upper

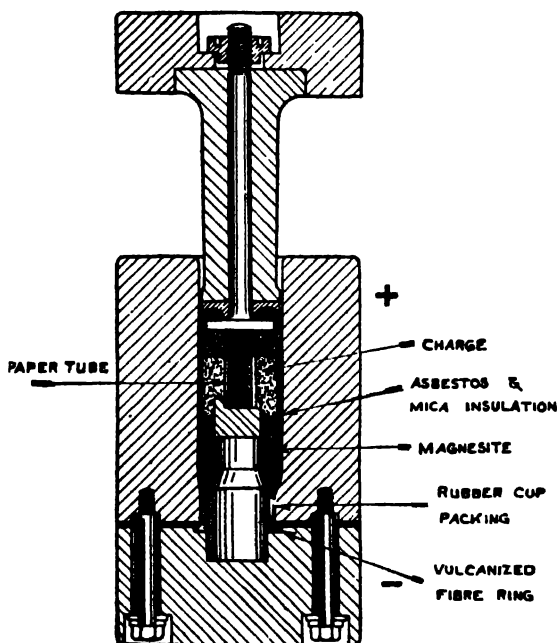


FIG. 6.

end of the conductor by a layer of graphite which rests on the charge under treatment. The bottom end of the conductor rests on or is spigoted into a cast-iron block which rests on the bottom pole; this block is sometimes partially melted, but can be easily renewed. The container is charged by first stemming magnesite powder by hand around the bottom pole piece and block; then the charge is placed on the top and pressed to 5 tons per square inch; the top ram is then removed and a hole drilled through the charge and the container inserted; liquids if used, or carbon dioxide snow, may then be

introduced ; lastly, a layer of graphite is placed on the top and the whole pressed to the desired pressure for the experiment.

In one experiment several pounds of carbon dioxide snow were added to the charge, which consisted of magnesia, and was so arranged that evaporation of the heating carbon rod took place in an atmosphere of carbon dioxide and carbon monoxide under a gaseous pressure of 4400 atmospheres, the condensate resulting being soft graphite. Upwards of 200 chemical reactions arranged to deposit carbon were tested under high pressure and central heating. After each experiment samples were taken from various parts of the charge and carefully analysed for diamond, the methods of the analyses generally following those of Moissan and Crookes. Very small residues of diamond occasionally occurred, but they

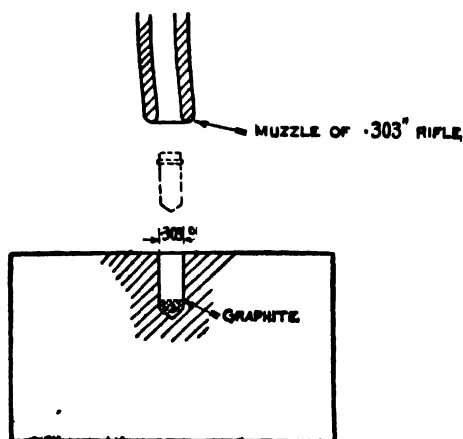


FIG. 7.

appeared to be associated with the presence of iron in the charge, whether introduced intentionally or from the melting of the pole pieces, short circuits, or from other causes. On the whole there was no evidence that diamond had been produced by any of the chemical reactions, some of which were endothermic, such as carborundum and sodium carbonate, which produced a grey solid which detonated when struck with a hammer, and nearly caused a serious accident. In one experiment the charge was olivine and water ; when molten under 10 tons per square inch, the pressure was suddenly removed and artificial pumice was formed by the expansion of water vapour absorbed by the olivine when molten. Having nearly reached the limits of steady pressure obtainable in steel containers under a press, experiments with impact pressures produced by steel bullets were

tried which produced much higher instantaneous pressures than are obtainable in any die.

A rifle 0.303 inch bore was arranged for withstanding a charge of cordite 90 per cent. in excess of the service charge.

The gun (Fig. 7) was fixed with its muzzle 6 inches from a massive block of steel, in which a hole 0.303 inch in diameter had been drilled to a depth somewhat greater than the length of the bullet, and in alignment with the bore of the gun; cylindrical bullets of steel with a copper driving band were chiefly used, shorter than the service bullet, and about one-half of the weight. The substance to be compressed was placed either at the bottom of the hole, when a conical-nosed bullet of mild steel was used, or over the

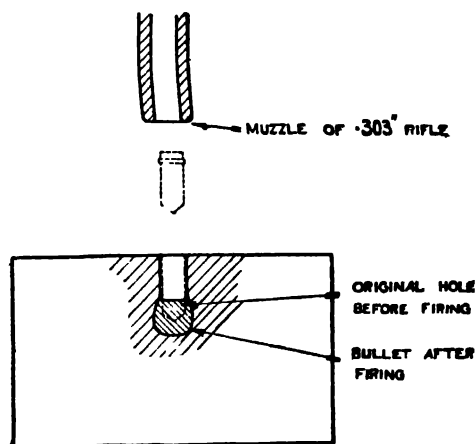


FIG. 8.

mouth of the hole, when a cupped-nose bullet of tool steel was employed. About one hundred experiments were made.

The substances tested included graphite, sugar carbon, bisulphide of carbon, oils, etc., graphite and sodium nitrate, graphite and fulminate of mercury, finely divided iron and fine carborundum, olivine and graphite, etc. After each shot the bullet and surrounding steel were drilled out, and the chips and entrained matter analysed. Fig. 8 shows the bullet in the hole after firing.

Several experiments were also made with a bridge of arc light carbon placed over the hole and raised to the limit of incandescence by an electric current, and the shot fired through it into the hole at the moment the carbon commenced to vaporize, as observed in a mirror from without. Also an arc between two carbons was arranged to play just over the hole, and the shot fired through it (Fig. 9).

The residues were in all cases exceedingly small, and there was no evidence of any incipient transformation of carbon in bulk into diamond that could be detected by analysis.

The pressure on impact of a steel bullet fired into a hole in a steel block which it fits is limited by the co-efficient of compressibility of steel; with a velocity of 5000 feet seconds it is about 2000 tons per square inch. Measurements made from a section through the block and bullet (Fig. 8) showed that the mean retardation on the frontal face after the impact till it had come to rest was about 600 tons per square inch. Several experiments were made by substituting a tungsten steel block hardened and tempered and a hole tapering gently from 0.303 inch at the mouth to 0.125 inch at the bottom. The mild steel bullet was deformed by the tapered hole, which greatly increased the velocity imparted to the nose. Progressively increased charges were used. With the 90 per cent. excess charge the block always split on the first shot, but this probably

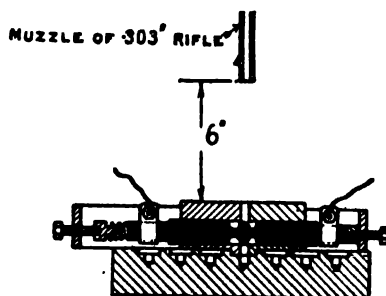


FIG. 9.

occurred after impact, and not till the full instantaneous pressure had been exerted, which was probably about 5000 tons per square inch, or about equal to that at the centre of the earth.

It would be interesting to repeat some of these experiments on a larger scale. With a projectile of 6 inches or 9 inches in diameter and a velocity of 5000 feet seconds, the instantaneous pressure would be the same, but its duration (which is proportional to the linear dimensions) would be increased from 20 to 80 fold. It has been estimated that the rise in temperature due to adiabatic compression of incandescent carbon when subjected to 2000 tons per square inch is of the order of about 1000° C., so that actual melting of the carbon would probably have occurred when the shot was fired through the incandescent carbon bridge.

Another experiment was arranged which would ensure that carbon should be subjected to an extremely high temperature concurrently with high pressures, obtained by the rapid compression of the hottest

possible flame, that of acetylene and oxygen, with a slight excess of the former to provide the carbon. The arrangement was as follows (Figs. 10 and 11):—A very light piston made of tool steel was carefully fitted to the barrel of the gun of 0·9-inch bore; the piston was flat in front, lightened out behind, and fitted with a cupped copper gas check ring, the cup facing forward; the total travel of the piston was 36 inches. To the muzzle of the gun was fitted a prolongation of the barrel formed out of a massive steel block, the joint being gas-

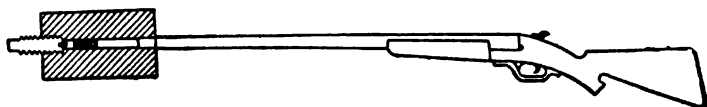


FIG. 10.

tight; the end of the bore in the block was closed by a screwed-in plug made of tempered tool steel, also with a gas-tight collar. A small copper pin projected from the centre of the plug to give a record of the limit of travel of the piston. The gun was loaded with 2 drachms of black sporting powder, which amount had been calculated from preliminary trials. The barrel in front of the piston was filled with the mixture of acetylene and oxygen. It was estimated

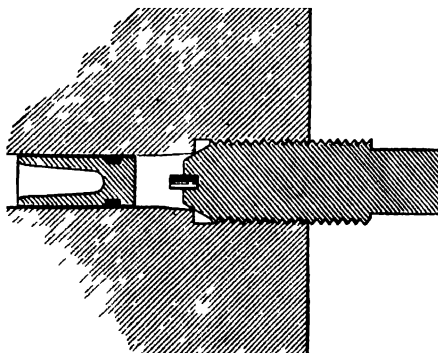


FIG. 11.

that this mixture would explode when the piston had travelled about half way along the bore; when fired the piston travelled to within $\frac{1}{8}$ inch of the end, as had been estimated, giving a total compression ratio of 288 to 1. As a result it was found that the surfaces of the end plug, the fore end of the piston, and the circumference of the bore up to $\frac{3}{8}$ inch from the end of the plug had been fused to a depth of about 0·01 inch, and were glass hard; the surface of the copper pin had been vaporized, and copper sprayed over the face of

the end plug and piston. The end plug, which had been hardened and tempered to straw colour, showed signs of compression, and the bore of the block for $\frac{3}{8}$ inch from the plug was enlarged by 0.023 inch in diameter, both indicating that a pressure above 100 tons per square inch had been reached.

A little brown amorphous carbon was found in the chamber, which was easily destroyed by boiling sulphuric acid and nitre. There was no diamond residue from this. Considering the light weight of the piston and the very short duration of the exposure to heat, the effects would indicate that a very abnormal temperature had been reached, many times greater than exists in the chambers of large guns. A calculation made by Mr. Stanley Cook, based upon the ratio of compression and a final pressure of 15,000 atmospheres, indicates that a temperature of between 15,250° C. and 17,700° C. was reached, the exact temperature depending upon the amount of dissociation or combination existing between the elements at the time.

CALCULATION OF THE TEMPERATURE REACHED ON THE COMPRESSION OF ACETYLENE AND OXYGEN EXPERIMENT.

By Stanley S. Cook.

The temperature reached may be estimated from the final pressure, which the observed deformation of the block and plug indicates to have been in the neighbourhood of 100 tons per square inch. But it must be remembered that there is a change of molecular volume as a result of combustion. Thus the mixture, which as C_2H_2 and 5 (O) has $3\frac{1}{2}$ molecular volume, would on combustion to $2CO_2$ and H_2O have only 3 molecular volumes. The final temperature deduced from the pressure will therefore depend upon the extent to which chemical combination has taken place.

The original mixture being at atmospheric pressure and a temperature of 290° C. absolute, a pressure of 100 tons per square inch after compression to $\frac{2}{3}\frac{1}{2}$ of its original volume would indicate a temperature of 15,250° C. If, however, complete combustion has taken place, this same pressure would correspond to a temperature greater in ratio of $3\frac{1}{2}$ to 3, viz. to 17,700° C. The actual temperature must therefore have been something between these two values.

Let us for a moment consider the pressures and temperatures possible in nature (in this I am indebted to kind assistance from Professor Jeans). The pressure at the centre of the earth is between 4000 and 10,000 tons per square inch, according to the variation in density of the concentric layers.

Emden has estimated the probable pressure at the centre of the

more massive component of the binary star S. Hercules to be 360,000,000 tons per square inch.

Again the densities of the brighter components of the stars of Cassiopeiæ and B 612 are estimated by Opik to be about that of iron; and if we assume their diameter to be the same as that of the sun, and that each has an initial velocity in space not greater than 30 miles per second, and that they directly collide, then, owing to their mutual attraction, Jeans calculates that their velocity will have increased to 450 miles per second, and the pressures in the centre as they strike and flatten would be of the order of 1,000,000,000 tons per square inch. He also estimates that the heat equivalent of the energy would be sufficient to vaporize the whole mass 100,000 times over. This immense pressure would be maintained for many minutes, perhaps for half an hour.

Let us consider what is the greatest pressure that can be produced artificially. If the German gun which bombarded Paris were loaded with a solid steel projectile, somewhat shorter and lighter than the one actually used, a muzzle velocity of about 6000 feet seconds might be reached (many years ago Sir Andrew Noble had reached 5000 feet seconds); and if it was fired into a tapered hole as I have described in a large block of steel, this would give the greatest instantaneous pressure that can be produced artificially, as far as we at present know, viz. about 7000 tons per square inch. This is only about 1-150,000 part of that possible by the collision of the largest stars.

As to the temperature and conditions of matter under these intense pressures extrapolation from known data is valueless. We have no knowledge of the co-efficients of compressibility of matter under these conditions, or of its specific heat—what may be the effect on the atom, and will elements under such conditions be transformed into others of higher atomic weight?

Some of us may recall that in 1888 the lecturer, after describing in this room the experiment in which oxygen at atmospheric pressure was passed in close contact with a platinum surface heated by the oxyhydrogen burner to nearly its melting point, and then immediately cooled by contact in water, said: "In this experiment ozone is formed by the action of a high temperature, owing to the dissociation of the oxygen molecules and their partial recombination into the more complex molecules of ozone. We may conceive it not improbable that some of the elementary bodies might be formed somewhat like the ozone in the above experiment, but at very high temperatures, by the collocation of certain dissociated constituents and with the simultaneous absorption of heat."

It seems indeed probable that the centres of the great stars and stars in collision may be the laboratories where the elements as they gradually degenerate are being continually regenerated into others of higher intrinsic energy, and where endothermic processes such as the

recombination of lead and helium into radium may be taking place, absorbing in this process an energy of $2\frac{1}{2}$ million times that developed by the explosion of an equal weight of T.N.T.

The transformation of only a minute fraction of the mass of two colliding stars would therefore be amply sufficient to absorb the whole energy of their collision.

Emerson said many years ago, "None but the elements can themselves destroy."

[C. P.]

Friday, May 7, 1920.

SIR JAMES REID, BART., G.C.V.O. K.C.B. M.D. LL.D.,
Vice-President, in the Chair.

THE RIGHT HON. LORD RAYLEIGH, Sc.D. F.R.S. M.R.I.,
Professor of Physics, Imperial College of Science.

The Blue Sky and the Optical Properties of Air.

Scattering by Small Particles. Polarisation.

THE subject chosen for this evening is one which specially interested my father throughout his career. I shall try to put before you some of his conclusions, and then pass on to more recent developments, in which I have myself had a share.

Let us begin with one of his experiments which illustrates the accepted theory of the blue sky. We have here a glass tank containing a dilute solution of sodium thiosulphate. A condensed beam from the electric arc traverses it and then falls on a white screen, where it shows the usual white colour. I now add a small quantity of acid, which decomposes the solution with slow precipitation of very finely divided particles of sulphur. As soon as this precipitation begins you see that light is scattered—that is to say, that it is diverted to every side out of the original direction of propagation. Moreover, you will observe that the scattered light is blue. The transmitted beam is robbed of its bluer constituents, and tends to become yellower, as you may see on the screen.

The light scattered laterally is to be compared to the blue sky; the yellow transmitted light to the direct light of the setting sun, when it has traversed a great thickness of air.

As the precipitation goes on, the transmitted light becomes orange, and even red. But the particles of sulphur eventually get bigger, and then give a less pure blue in the lateral direction. We shall have more than enough to occupy us if we confine our attention to the earlier stages, when the particles are small compared with the waves of light.

A very important property of the scattered light is its polarisation. The vibrations of the scattered light as you have seen it, viewed laterally in the horizontal plane, are almost wholly up and down. No light is emitted which vibrates in the horizontal plane. It is easy for individual observers to verify this with a Nicol's prism held

to the eye, but this direct method unfortunately does not lend itself to public demonstration.

We may, however, use polarised light to begin with, and you can then observe that if the polarising Nicol is set so as to transmit up and down vibrations, these are abundantly scattered towards you by the small particles. As I turn the polarising Nicol through a right angle, you will see that the light scattered towards you is extinguished.

The polarisation of light scattered by the sulphur particles is one of the most conclusive reasons for considering it to be an analogue of the blue light of the sky, for the latter shows a polarisation of exactly the same kind when examined at right angles to the sun.

A cloud of small particles of any kind is capable of producing these effects, the essential condition being that the individual particles should be of small dimensions compared with the wave-length of light, so that at a given moment the vibration at a given particle may be regarded as having a definite phase. In this case it was shown by my father that the shorter (blue) waves are of necessity more scattered than the longer ones (red); thus the scattered light is bluer than the original. This conclusion can be justified in detail whether we adopt the elastic solid theory, or the electro-magnetic theory of the nature of light, but it is also deducible from the general theory of dimensions, without entering upon any details of the nature of light beyond its characterisation by the wave-length.

An alternative theory which still sometimes shows its head, attributes the colour of the sky to a blueness of the air, regarded as an absorptive medium. Such blueness is referred to the presence of ozone, and appeal is made to the undoubted fact that a sufficiently thick layer of ozone shows a blue colour by absorption. This theory gives no account of why the sky light is polarised, or indeed of why there is any light in the clear sky at all. Further, its fundamental postulate that the air is blue by transmission is contrary to observation. The setting sun is seen through a greater thickness of air than the midday sun. According to the theory under discussion, the setting sun ought to be the bluer of the two, which everyone knows it is not. No doubt the presence of ozone tends to make the air blue by transmission. But this effect is more than compensated by the lateral leakage (scattering) of blue light from the beam, which makes the transmitted light yellow.

Dusty Air and Pure Air.

If it be conceded that the blue sky is due to scattering by small particles, we are confronted with the question of what nature are these particles? At the time of my father's early investigations (1871) this was left open, though they were regarded as extraneous to the air itself. In 1899 he returned to the subject, and considered the matter from the point of view of what was lost by the original beam

by lateral leakage (scattering), which simulates the effect of absorption. He then found that the air itself, regarded as an assemblage of small particles (molecules of oxygen and nitrogen), would have an apparent absorbing power not much less than that actually deduced by observations of the sun at different altitudes. The inference was that the air itself was capable of accounting for much, if not all, of the scattering which is observed in the blue sky; in fact that the molecules of air are the small particles in question.

When a beam of sunlight enters a room through a small aperture in the shutter, its course is readily traced by the brightly illuminated motes in the air. Prof. Tyndall, working in this Institution, devoted much attention to the nature of these motes, and the methods by which they may be got rid of. His results may be consulted in the fascinating essay on "Floating Matter." One way of getting rid of the motes is to filter the air through cotton wool. We have here one of Tyndall's own experimental tubes. The electric beam passes axially along it, and is concentrated to a focus about the middle of the length. Its track is conspicuous. If now we displace the air originally in the tube by filtered air, you see that the cone of light fades into invisibility.

Another of Tyndall's experiments was merely to place a spirit-lamp or Bunsen burner under the beam. Since most of the dust particles are combustible, the gases rising from the flame are free from them. As you now see, dark rifts appear in the beam where the uprising stream of dust-free gases traverses it.

Tyndall, on the strength of these experiments, stated without qualification that dust-free air does not scatter light, but my father's views and theory lead clearly to the conclusion that it does. But when I asked him what he thought about the feasibility of detecting it by a laboratory experiment, he was not very sanguine of success. It seemed worth while, however, to make the attempt, and I came to the conclusion that the difficulty was not so much in the faintness of the effect to be looked for as in the avoidance of stray light which came into competition with it. The essential thing is to get a perfectly black background against which the beam (viewed transversely) can be observed. We cannot get this with a vessel like Tyndall's tube, just used. It is necessary to have what may be called a black cave, and to view the beam as it crosses in front of the mouth of the cave, the latter forming the background. If the cave is deep enough, there is no limit to the blackness attainable. The great sensitiveness of the well-rested eye, or the photographic plate, can then be brought to bear, and the track of the beam can be well seen, however carefully the dust is removed.

Some persons have been inclined to question whether the dust is removed completely in these experiments. As a matter of fact this is not where the difficulty lies at all. Dust so fine as to be very difficult of filtration is an arm-chair conception, not encountered in

practical experimenting. An enormous multiplication of the length and tightness of the cotton-wool filter makes no difference at all; a filter of modest dimensions doing all there is to do.

The dust particles which are originally present in the air, near the ground or in a room, are large, being in some cases individually visible to the naked eye; thus they do not fulfil the condition for scattering a preponderance of blue light. The molecules of air are of course amply small enough, and the band of light seen stretching across the mouth of the dark cave is, to my eyes at least, of a full blue colour. In exhibiting the effect to individual friends (and unfortunately it is not bright enough to be shown to an audience), I have been surprised and somewhat disconcerted to find that they do not all see it blue as I do, but some, for example, describe it as lavender. This is undoubtedly due to a peculiarity of colour-vision where faint lights are concerned. The ultimate test is the spectro-scope. Photographs of the scattered light taken with this instrument clearly show that the maximum of intensity is shifted towards the blue, as compared with the original exciting light.

Polarisation of Light Scattered by Pure Air.

A very important point to examine in connection with the scattered light is its state of polarisation. Visual examination with a Nicol's prism soon showed that the polarisation was very nearly complete. For closer examination I had recourse to photography. It may perhaps be thought an easier and more effective plan to look at a phenomenon than to photograph it, and no doubt it is so in many cases; not however where the light is very faint, but admits of long exposure. It has long been recognised that photographs of the nebulæ will show much more than can be detected visually by the keenest and most discriminating eye. In this work on the scattering of light, I have found it positively less trouble to take a photograph than to make a visual observation, even when the latter was feasible. The time required to rest the eye in darkness and the effort of attention required in observing a faint effect cost the experimenter more effort than the exposure and development of a plate.

When the scattered beam in pure air is photographed, with a double image prism of Iceland spar mounted over the photographic lens, it is found that the polarisation is nearly complete, but not absolutely so. However carefully the instrumental adjustments are made, and however carefully the air is filtered, I have found that there is a slight residual polarisation indicating vibrations parallel to the direction of the original beam. The intensity of this residual polarisation, in what may be called for convenience the wrong direction, is about 4 per cent. of the whole. Now, as the theory shows, there are two causes to which failure of complete polarisation may be attributed. One, which we may dismiss in this case, is that the

particles are not small enough. Another is that they are not spherical—that is to say, that it is not a matter of indifference which way they are presented to the primary beam. The latter alternative may be illustrated by considering an extreme case—namely, what we may call a needle-like molecule, capable of vibrating only in one direction fixed within it. Evidently such a molecule when obliquely situated will have a component vibration parallel to the direction of the incident light.

From the experimental fact that there is such a component, we may infer that the molecules of air are not in the optical sense spherical. Experiments on various gases have shown a characteristic departure from complete polarisation, different for each gas. Much effort has been spent on determining the exact amount for each, and it is hoped that the numbers obtained will form valuable material in the future for investigating the structure of atoms and molecules.

Polarisation of the Night Sky.

We have seen that the polarisation of the daylight sky is one of the most conclusive proofs that its light is due to scattering by small particles. What of the sky at night? Some of you will perhaps be inclined to reply that the sky at night is dark, and that the question whether its light is polarised does not arise. It is, however, by no means the case that the sky on a clear night is absolutely dark, as anyone may readily prove by holding his hand with outstretched fingers against the sky. The fingers will appear dark against the sky as a luminous background.

The light is no doubt very faint, but I thought it would be practicable to test whether it was appreciably polarised or not. For this purpose what is called a Savart polariscope was used. Time will not allow us to consider the rather complex theory of this apparatus; it must suffice to say that if the light which falls upon it contains even a small part which is polarised, alternately bright and dark bands are produced, which further show colour due to the composite nature of white light. These bands are clearest when the incident light is completely polarised, as you now see them projected on the screen. But they can still be seen when the polarisation is but slight. I will illustrate this by removing the polarising Nicol which I have been using, and substituting a single glass plate, through which the incident light passes. If I incline this plate, so as to polarise a small fraction of the light, you see the bands, faint but sufficiently distinct. In examining the light of the night sky, a photographic plate is substituted for the paper screen I have been using to-night, and the apparatus is designed for the utmost economy of light. With two hours' exposure a definite image of the sky was obtained, with the stars superposed upon it. The Savart bands could be seen, but they were very faint compared with what

would have been observed with an equally good image of the daylight sky. The part of the sky examined was near the pole, and therefore nearly at right angles to the sun. If, as seemed possible, the night sky derived its light from an attenuated atmosphere so high as to be outside the earth's shadow, we should expect it to show the same polarisation as the day sky. Since it does not do so, we must attribute the light at night to some different origin.

I was fortunate in being able to interest Prof. Hale in this matter while he was on a visit to England, and as a result Mr. Babcock repeated the observations in a modified form at the Mount Wilson Observatory in California. The traces of polarisation which he obtained in that clear atmosphere were even less than what I got in England.

Ozone, and the Limit of the Solar Spectrum.

Although, as we have seen, the idea that the blue colour of the sky is due to any action of ozone cannot be admitted, yet there are points of great optical interest connected with the presence of this gas in the atmosphere. We may now turn to the consideration of some of these.

It is of course well known that when the solar spectrum is formed by a prism of quartz, or by a grating, the spectrum can be observed to extend beyond its visible limit in the violet into the region called ultra-violet. When, however, we examine the spectrum of an electric arc (and for this purpose an iron arc is particularly suitable), the extension is observed to be very much greater than in the solar spectrum. This is not because the sun does not emit any rays of the kind in question, but because the earth's atmosphere will not allow them to pass through so as to reach us at the earth's surface. There are many reasons for feeling sure that this is the true explanation, but one of the simplest will here suffice. When the sun is near the horizon, so that the rays pass obliquely through the earth's atmosphere, and consequently have to traverse a thicker absorbing layer, the extent of the ultra-violet spectrum is found to be even less than when the sun is high and less air is traversed by the rays. This sufficiently proves the point.

It has long been suspected that ozone in the atmosphere is the effective cause of this absorption of the ultra-violet rays. The most important constituents of air, oxygen and nitrogen, do not appreciably absorb at the point where the solar spectrum ends, nor do the constituents of secondary importance, carbonic acid, water-vapour and argon. We must therefore look to some rare constituent of air which is very opaque to this region of the spectrum. Ozone possesses this opacity, as I shall now show you. So far as I know it has not been attempted to show this before to an audience, but I think you will be able to see it without difficulty. As a source of light an iron arc is used, and the lenses and prism used in forming the

spectrum are of quartz. I allow the spectrum to fall on a piece of paper, and you see the usual succession of colours, red, yellow, green, blue and violet, forming a comparatively narrow rainbow-like band. Beyond the violet all appears dark, the eye being insensitive to the ultra-violet rays. If now I substitute for the paper a screen of barium platinocyanide * (of the kind used in X-ray work), we see an immense extension of the spectrum beyond the violet. The screen has the property of transforming the ultra-violet rays, which the eye cannot detect, into green rays which are readily visible. Thus beyond the violet region we see green, which is, of course, in no way to be confused with the original green which was present in the source, and appears in its normal position in the spectrum, on the other side of the blue-violet. I interpose a thin sheet of ordinary glass, and the greater part of this extension of the spectrum which we get on the fluorescent screen disappears. What I want specially to show you, however, is that a thin layer of ozone, much too thin to have any perceptible colour, will have the same effect. There is a glass tube, about 6 inches long and $\frac{3}{4}$ -inch diameter, situated between the quartz lantern condenser and the slit, when the beam is parallel, and the walls of the tube are projected as two thin transverse lines on the slit, dividing the spectrum into thin horizontal strips, one over the other. The light constituting the middle strip has traversed the tube, but the light constituting the upper and lower strip has traversed the open air above and below the tube. A stream of oxygen passes through a Siemens' ozone generator and enters the middle of the observation tube, streaming out at the two ends. While the ozone generator is not excited, the middle strip of the spectrum is similar to the comparison strips above and below. If the induction coil is turned on so that ozone passes into the tube, you see that in a few seconds the greater part of the ultra-violet spectrum fades out from the middle strip, which contrasts sharply with the upper and lower ones. When the coil is turned off, the ozone is rapidly blown out by unozonised oxygen, and the original state of things restored.

It must be remembered that the ozone used in this experiment is extremely dilute, probably only a fraction of 1 per cent. of the oxygen in the tube. Yet it interposes an impassable obstacle to the ultra-violet rays, at least to those of shorter wave-length than about 2900 Ångströms. It cuts off the iron spectrum at about the same point where the solar spectrum ends. Speaking roughly and generally, it may be said that glass is somewhat more opaque than ozone, i.e. that with diminishing wave-length the limit of transmission is reached somewhat sooner. To make a statement of this kind quite definite the thickness must of course be specified.

Sir William Huggins devoted a great deal of attention to the

spectra of the sun and stars in the extreme ultra-violet region, using for the purpose a reflecting telescope, and prisms and lenses made of quartz or Iceland spar. In this way the absorption of a glass objective was avoided. He noticed in 1890 that the spectrum of Sirius showed a number of bands near the extreme limit of atmospheric transmission, the bands tailing off into complete absorption.

These bands were observed and discussed by other authors, but no definite conclusion was reached as to their origin until 1917, when the matter was taken up by my colleague, Prof. Fowler, and myself. Our interest was stimulated by an excellent photograph of the bands, taken at Edinburgh Observatory under Prof. Sampson's direction, which I show on the screen. We found that the same bands were present in the solar spectrum. It may seem strange that this had not been observed long ago, considering how closely the solar spectrum has been scrutinised for more than a generation. As a matter of fact this is one of the cases where a powerful instrument is a positive disadvantage. The bands are diffuse, and under high dispersion they are unrecognisable. In any case they are less conspicuous than in the spectrum of Sirius, because in the sun numerous metallic lines are superposed upon them and distract the eye.

Now the position and general aspect of these bands suggested that they were connected with the absorption which terminates the spectrum. This led us to suspect that they were due to ozone, and the suspicion was readily confirmed by experiment. Burning magnesium ribbon gives a convenient source of continuous spectrum in the ultra-violet region. Interposing a long tube containing ozone between the burning magnesium and the slit, a series of bands was photographed which exactly corresponded to those photographed in the solar spectrum with the same instrument, as you will see in the slide shown.

Absence of Ozone Near the Ground.

We are driven then to the conclusion that the absence of short waves from the spectra of the sun and stars is due to absorption by terrestrial ozone. But it was not thought desirable to let the matter rest there. It is true that many attempts had been made to determine the (no doubt very small) quantity of ozone in air by chemical means, but with very conflicting results, because other constituents of air, such as oxides of nitrogen, are liable to produce reactions not unlike those of ozone. It seemed more satisfactory to test the absorbing power of air near the ground for ultra-violet rays, to which ozone is so opaque. I used for this purpose a mercury vapour lamp in a quartz vessel, which is a powerful source of ultra-violet rays, and observed its spectrum four miles away, so that the mass of air intervening was as great as that between the midday summer sun and the top of the Peak of Teneriffe, from which observations of the extent of the solar spectrum have been made. The result was to

show that the mercury lamp spectrum was by no means stopped when the solar spectrum stops, but that it extended to the region where ozone is most opaque. There is a strong mercury line (wave-length 2536) at about this point which was distinctly photographed. Its intensity was of course a good deal reduced relative to the visible spectrum by atmospheric scattering. But there was no evidence whatever of ozone absorption.

What conclusion can we draw? Evidently that the absorbent layer of ozone in the air is high up, and that there is little or none near the ground. It may seem at first sight that this thin and inaccessible layer of ozone, of which we have learned by a chain of reasoning not less conclusive than direct observation, is a matter of little importance to man and his welfare. There could be no greater mistake. It acts as a screen to protect us from the ultra-violet rays of the sun, which without such a protection would probably be fatal to our eyesight, at least if one may judge from the painful results of even a short exposure to such rays, which those who have experienced it are not likely to forget.

[R.]

Friday, May 28, 1920.

SIR JAMES CRICHTON-BROWNE, J.P. M.D. I.L.D. D.Sc. F.R.S.,
Treasurer and Vice-President, in the Chair.

W. LAWRENCE BRAGG, M.A., Langworthy Professor of Physics,
Manchester University.

Crystal Structure.

1. THE examination of the structure of crystals by means of X-rays has made it possible to discover the arrangement of the atoms in a number of the simpler crystal forms. We owe to Laue the original experiments, first published in June, 1912, which placed this power in our hands. In seeking for some means of diffracting X-rays and thus investigating their nature, he was led to use a crystal as a diffraction grating for the rays, the regular arrangement of the atoms in the crystal structure performing the same function as the lines ruled on a grating. The success of his experiment has resulted in investigations which have vastly increased our knowledge of X-rays, of crystal structure, and of the structure of the atom itself.

The problem of crystal structure, which forms the subject of this Discourse, has been attacked in various ways. In his original work Laue obtained diffraction patterns by passing a fine beam of X-rays through a thin plate of crystal, and allowing the diffracted beams to fall on a photographic plate which recorded their geometrical distribution. Though this clearly showed that the X-rays consisted of electromagnetic waves of very short wave-length, diffracted by the atoms of the crystal, the complexity of the resulting pattern on the photographic plate made it difficult to draw conclusions as to the arrangement of the diffracting atoms. A simpler method of attack was realized in the X-ray Spectrometer devised in 1913 by Sir W. H. Bragg. In the course of experiments with which the author was associated, the structure of crystals such as diamond, sodium chloride, zincblende, fluor spar, and the carbonates of the divalent metals were fully worked out, the arrangement of the atoms being determined.

Large crystals are necessary for these methods of analysis, and in order to examine crystalline substances which could not be obtained except as a mass of minute crystals, Debye employed another experimental arrangement which he published in December, 1915. Instead of using a single crystal, Debye passed the X-rays through a mass of finely-powdered material, consisting of crystalline fragments oriented in

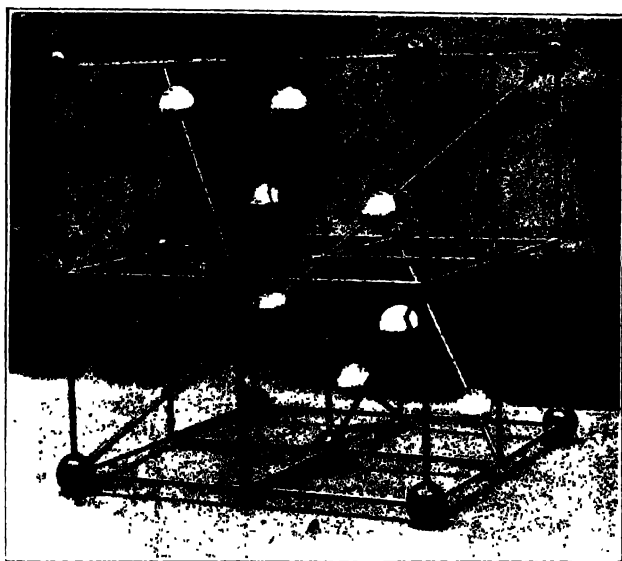


FIG. a.—Structure of Iron pyrites, FeS_2 .

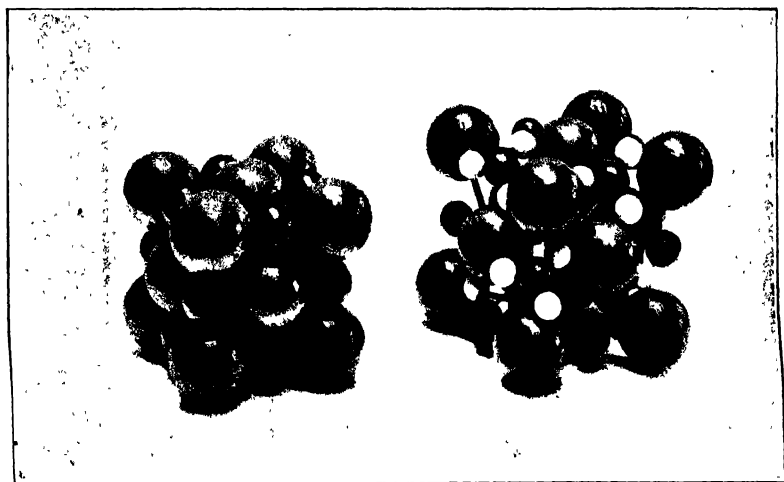
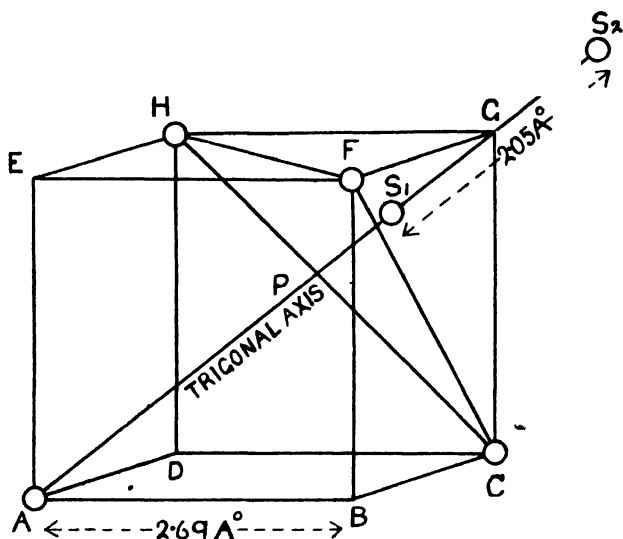


FIG. b.—Potassium chlorido, KCl ; Calcium carbonate, CaCO_3 .

all directions, the diffraction of the X-rays resulting in the appearance of a set of "halo" rings on a suitably placed photographic plate. He analysed graphite, and showed that so-called "amorphous" carbon consists in reality of minute graphite crystals. The arrangement of the atoms in silicon, tungsten, tin, gold, aluminium and other elements has been discovered by Debye's method. Sherrer has found that colloidal gold and silver consist of minute crystals, the dimensions of which are so small that they are only four or five atoms deep in any direction, and which yet retain exactly the same crystal structure as massive gold and silver. The same method was arrived at inde-



UNIT OF IRON PYRITES STRUCTURE

FIG. 1.

pendently by Hull, and he has extended it to a number of interesting crystals. We now know the atomic arrangement for a very large proportion of the crystalline elements and simple compounds.

2. The essential principle of these methods of crystal analysis may be compared to that involved when a diffraction grating is calibrated by means of monochromatic light, the wave-length of which is known accurately. By finding the angle at which the light is diffracted by the grating, the distance apart of the lines ruled on the grating can be calculated. The planes on which the atoms of a crystal are arranged correspond to the lines of a diffraction grating. A beam

of X-rays of known wave-length falls on the crystal, and it is found that when the beam makes a certain glancing angle with the planes of the structure it is strongly diffracted. By measuring this angle it is possible to calculate the distance between the planes of the crystal structure, just as the distance between the lines of the grating is obtained by employing monochromatic light. The distance between the planes in all directions is thus measured up, and leads to the fixing of the atoms in the crystal structure at their intersections. In this way the crystalline arrangements of some twenty or thirty elements, of compounds such as NaCl , MgO , ZnS , the carbonates, the

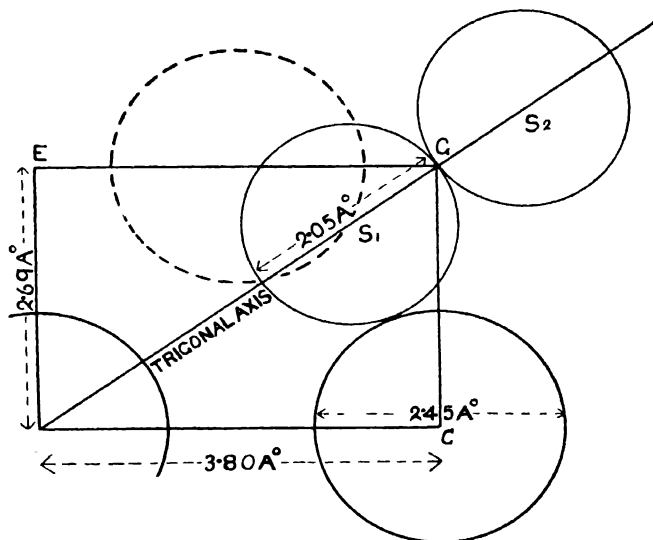


FIG. 2.

spinel group of minerals, the alums, the oxides isomorphous with ruby, pyrites, fluor, galena and many others have been analysed.

3. In many simple crystalline substances the atoms are so arranged that their exact positions are determined by the symmetry of the crystal. In the diamond, for example, each carbon atom is at the centre of four other carbon atoms. In the cubic crystal of potassium chloride, the atoms are arranged so that potassium and chlorine atoms alternate at the corners of the cubes in the structure. Every potassium atom is surrounded symmetrically by six chlorine atoms, every chlorine atom by six potassium atoms. The atoms cannot be displaced

from these positions without destroying the symmetry of the structure, and their exact positions are therefore defined. Such structures are illustrated by the models of potassium chloride and zincblende in Plates I. and II.

In contrast to this, the positions of the sulphur atoms in the crystal of iron pyrites, FeS_2 , are defined by symmetry alone. Plate I., fig. *a*, and Figs. 1 and 2 illustrate this structure. The sulphur atoms lie on certain axes of three-fold symmetry, illustrated by the model, and every atom occupies the same relative position along the appropriate axis, but this position must be determined by quantitative investigations of the diffraction of the rays. The ratio of the parts into which the cube axis is divided by the centre of the sulphur atom may be taken as the parameter fixing its position, and this parameter may have any value. In the case of the ruby, Al_2O_3 , two parameters are necessary to define the crystal structure; in quartz, SiO_2 , four parameters must be determined. The complexity of the crystal structure, and the difficulty of analysing it, increase greatly with the number of these parameters, and it is this which has limited to the simpler forms the types of crystal so far worked out.

4. In trying to find some method of simplifying the analysis of these complex structures, the author has been led to a manner of regarding the crystalline structure which is similar to the well-known theory proposed in 1906 by Barlow and Pope. Barlow and Pope pictured the atoms of a crystal as an assemblage of spheres, packed together tightly, the volume of the space in the crystal structure occupied by the sphere representing any atom being proportional to the valency of the atom. We now know the atomic arrangement of a number of crystals, and we know that the disposition of the atoms predicted by the "Valency Volume" theory, though in some cases it has been found to hold, is in general different to that which the X-rays have enabled us to discover. Nevertheless, Barlow and Pope's models of crystal structures may be modified so as to apply to crystals by substituting, for the valency volume law, one which assigns to the sphere representing any atom a constant size characteristic of that atom.

5. This may be illustrated by the iron pyrites structure already referred to. In this structure the iron atoms are situated on a face-centred cubic lattice. If the unit cube of this lattice be subdivided into eight cubes of half the linear dimensions, each of these latter will have an iron atom situated at four of its eight corners. Fig. 1 represents such a unit of the structure, the iron atoms being at the corners of A, C, H and F. One diagonal of each cube, the diagonal AG in the figure, is an axis of threefold symmetry, and the sulphur atom lies at some position along this axis. Since each corner of the cube is a centre of symmetry, there will correspond to the sulphur atom centred at S_1 a similar atom at S_2 , where $S_1G = S_2G$. A pair of sulphur atoms are thus associated with each cube corner, since one

threefold axis passes through every corner, and the necessary proportion of two sulphur atoms to one iron atom is realized.

On the conception of the crystal as a set of spheres packed together, it will be seen that there are two possible positions for the sulphur atom. It may lie at the centre of the cube, where it is surrounded by the four iron atoms at A, C, H, and F, an arrangement which exists in the structure of fluor spar, CaF_2 . Alternatively, it may move along the axis to a position G_1 on the other side of the plane HFC, where it will be packed between the three iron atoms at H, C and F, and the corresponding sulphur atom at S_2 .

If the size of the sphere representing the iron atom is known, geometrical considerations fix the centre of the sulphur atom touching the iron atoms and the other sulphur atom. As a first approximation to the size of the iron sphere, the distance between atomic centres in metallic iron, first analysed by Hull, may be taken. This distance is 2.47×10^{-8} cm., or 2.47 Ångstrom Units. Using this value, the ratio S_1G/AG is found to be equal to 0.22. The author originally deduced the value 0.20 for this parameter, and a more exact determination by Ewald gave it as 0.226, so it will be seen that the conception of the atoms as a set of spheres packed together leads to a determination of the parameter very near the true one. Further, the diameter of the sphere representing the sulphur atom follows to be 2.05 Å. Fig. 2 will illustrate the manner in which this result is arrived at.

6. The structure of zinc sulphide, and therefore the distance between the zinc and sulphur atomic centres, is known; it is illustrated by Plate II., fig. *a*. Taking the diameter of the sulphur sphere to be 2.05 Å, that of the zinc sphere touching it is found to be 2.65 Å. From the zinc oxide structure the dimensions of the oxygen sphere can be calculated; its diameter is found to be 1.30 Å. This difference of 0.75 Å between the diameters of the oxygen and sulphur spheres is also found to exist in a number of other crystals.

The rhombohedral carbonates typified by calcite, CaCO_3 , provide a check on these figures. We have seen that the oxygen sphere has a diameter of 1.30 Å. In the diamond the distance between the carbon centres is 1.54 Å, and this may be taken to be the diameter of the carbon sphere. Every carbon atom in the carbonates is closely surrounded by three oxygen atoms, and we should therefore expect the distance between carbon and oxygen centres to be $\frac{1}{2}(1.54 + 1.30)$ Å, or 1.42 Å. As a matter of fact the X-ray measurements show it to be 1.47 Å, which is in fair agreement with the calculated value. Further, in zinc carbonate the zinc atom is surrounded by six oxygen atoms, the distance between the centres being 1.99 Å. Comparing this with the distance 1.97 Å between zinc and oxygen

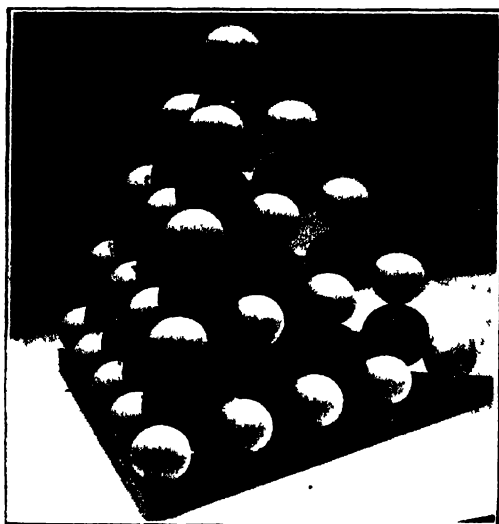


FIG. a.—Zincblende, ZnS

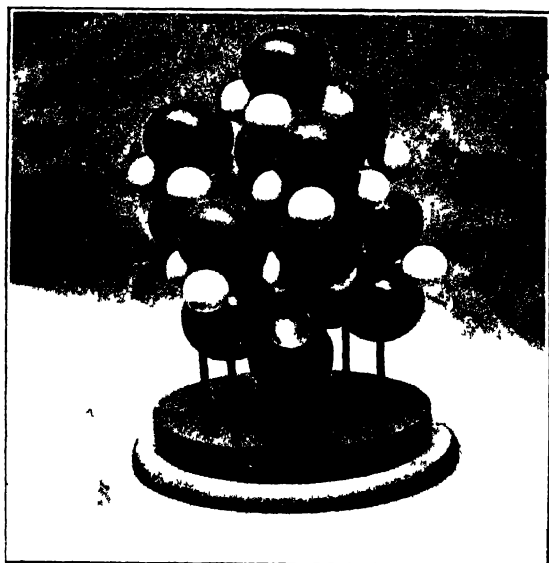


FIG. b —Alumina, Al_2O_3 .

centres in zinc oxide, we see that each of the atoms appears to occupy a space of the same dimensions in all these crystals, sulphur in pyrites and zinc sulphide, zinc in zinc sulphide, oxide, and carbonate, oxygen in zinc oxide and carbonate, carbon in the carbonate and in diamond.

7. This will illustrate the manner in which the atomic diameters shown in the diagram (Fig. 3) have been calculated. The results may be summarized by saying that the distance between two neighbouring atoms in a crystal structure is equal to the sum of two constants characteristic of the atoms. We can therefore picture the atoms as a set of spheres packed together so that they are in contact, by taking these constants to be the radii of the spheres, and the models which illustrate this lecture have been built up in this way.

In the figure the elements are arranged in the order of their atomic numbers, and the ordinates represent the diameters of the corresponding spheres, measured in Ångstrom Units. A comparison of the distances found between the atoms in these structures which have so far been determined, with the distance calculated by adding the "atomic radii," shows that the average discrepancy between the two is 0.06 Å, or between two and three per cent.

It will be seen that the atomic diameters lie on a series of regular curves which show very strongly the periodic arrangement of the elements. The monovalent electropositive elements have the greatest diameters, the divalent metals the next greatest, and passing along each period the diameter diminishes steadily until it approaches a lower limit for the electronegative elements at the end of the period. In the case of two of the elements, chromium and manganese, it is necessary to suppose that the atom has a smaller diameter when functioning as an electronegative element than as an electropositive one.

The curve may be compared to Lothar Meyer's curve of atomic volumes, but in the case considered above the volume is that occupied by the atom in all the compounds into which it enters, so that the curve has a wider application. The molecular volume of a compound often differs very greatly from the volume obtained by adding the atomic volumes of its constituents, but if the crystalline structure is taken into account, this generalization shows that the space occupied by each atom is approximately constant.

In some cases the distances between atoms do not agree with those calculated from the diameters; for example, this is the case for many of the elements. In spite of this, the analysis of a complicated crystal is greatly helped by this way of regarding the atomic arrangement. When marshalling the atoms together in trying to find some arrangements which account for the diffraction effects, the necessity of allowing each atom a certain space in the structure limits the variable parameters to a small range and so simplifies the analysis.

8. The physical interpretation of these empirical relations must be sought for in the structure of the atom, and in fact that theory of

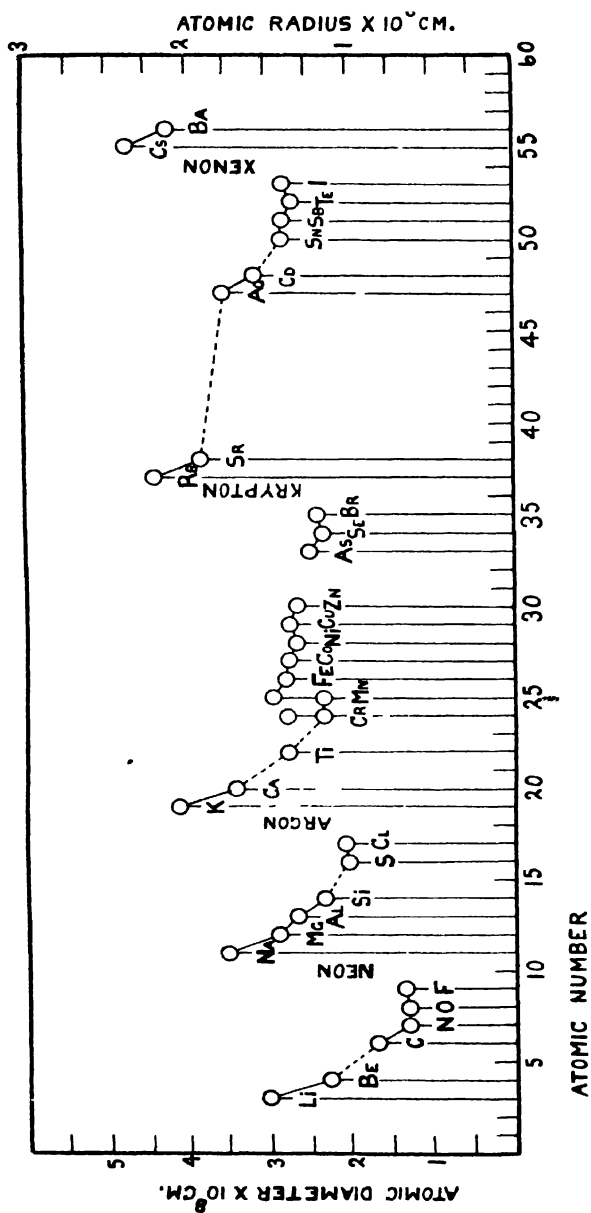


FIG. 3

atomic structure, which has been developed by the work of Kossel, Lewis, Born, Landé and many others, and which has been so strikingly summarized and extended recently by Langmuir, affords a ready explanation of the relationships. An essential feature of this theory is the supposition that the electrons, which surround the positive atomic nucleus, are fixed at, or oscillate about, certain definite positions in the atomic structure. This may be contrasted with the type of atomic structure represented by the Bohr atom, when the electronic orbits are supposed to enclose the atomic nucleus. In the "fixed electron" atom the electrons are placed in certain definite positions in a series of concentric spherical shells surrounding the nucleus. The commencement of each period of the periodic table marks the commencement of a new shell, and the inert gases which separate the periods are the atomic systems in which the outer shell has in each case its full complement of electrons.

The arrangement of electrons in an inert gas is a very stable one, corresponding to the chemical inactivity of the elements. The chemical properties of the other elements are due to the tendency of the system to revert to a more stable arrangement, such as that of one of the inert gases. Argon, for example, with atomic number 18 has a stable system of 18 electrons surrounding the nucleus. Potassium has an atomic number 19, and the nucleus is surrounded by 19 electrons in a neutral atom. There is, therefore, a tendency for the potassium atom to lose an electron and revert to the stable argon arrangement of 18 electrons, so that potassium behaves as a monovalent electropositive element. Chlorine, on the other hand, with atomic number 17, tends to gain an electron, and is a monovalent electronegative element. The atoms which have thus lost or gained an electron are positively and negatively charged; they are the kations and anions of potassium and chlorine.

The atomic numbers of the inert gases tell us the number of electrons in the outer shell which each atom must have for complete stability. The atomic numbers of helium, neon, argon, krypton, xenon and radon are 2, 10, 18, 36, 54 and 86, so that the number of electrons which must be added to complete each successive shell must be 2, 8, 8, 18, 18 and 32.

9. On this theory, two different types of chemical combination may be distinguished. The first is that represented by such a compound as potassium chloride. Here the potassium atom has lost an electron in reverting to the argon arrangement of eighteen electrons, and the chlorine atom has gained one. The oppositely charged ions are held together by the electrostatic attraction of their resultant charges. In the crystal of potassium chloride the positive potassium ion tends to surround itself with as many negative ions as possible. This is realized in the crystal structure (Plate I, fig. *b*), where each ion is surrounded by six of the opposite sign. The fact that the "molecule" of KCl has no apparent existence in the

crystal structure receives a natural explanation on this theory. The valency of the ion of either sign is due to an electrostatic attraction and can be subdivided to any extent.

The other type of chemical compound is that of two electronegative elements. Each element in this case has a smaller number of electrons than is necessary for complete stability. In order that the empty spaces in the outer shell may be completely filled, the atoms share electrons, the valency bonds corresponding to a pair of electrons held in common by both atoms. It is in this way of regarding the combination of electronegative elements that the Langmuir theory finds one of its strongest supports; the complicated valencies of elements such as nitrogen and phosphorus are readily explained by a consideration of the ways in which these atoms can fill up their outer shells by holding electrons in common with other atoms.

10. It has been seen that the potassium chloride crystal consists of alternate ions. The structure of calcite (Plate I, fig. *b*) presents the same alternation of ions, only in this case one of the ions, the CO_3 group, is complex. The calcium atom has lost two electrons in reverting to the argon arrangement of electrons, and it is therefore a doubly charged positive ion. The CO_3 group has absorbed into its system two additional electrons, and the four atoms in the group are surrounded by the total complement of electrons for stability, some of the electrons being held in common. In this crystal both types of chemical combination are illustrated: the calcium and O ions are held together by their charges; the carbon and oxygen atoms are bound together into the CO_3 group by holding electrons in common. The crystal is therefore divisible into units, each unit having a continuous outer electron shell. One unit is the calcium nucleus surrounded by its proper electron cloud, the other is the CO_3 group again surrounded by its electron cloud. Some repulsive force must be supposed to exist between the outer electrons which keeps the ions apart, opposing their electrostatic attractions for each other. The arrangement of the ions in potassium chloride and calcite is the same, except that in the latter case the substitution of the complex CO_3 ion for the Cl ion distorts the cube into a rhombohedron (cp. figure).

11. The empirical relations summarized by Fig. 3 can readily be interpreted on this theory. In calcium carbonate, for example, the proximity of the carbon and oxygen centres leads to a small diameter being assigned to the spheres representing these atoms, while the comparative isolation of the calcium atoms leads to a large diameter being taken for the corresponding sphere. We now see that the carbon and oxygen atoms are close together because they share electrons; the calcium atom is isolated because it has no electrons in common with the other atoms. The large diameter assigned to the electropositive elements does not therefore indicate that the outer electrons are any further from the nucleus than they are in the

electronegative elements of the same period ; it expresses the fact that the electropositive atom never shares electrons with the neighbouring atoms, and is therefore always found to be at a distance from the other atomic centres as if it occupied a large domain in the crystal structure.

12. In each period the divalent ion is assigned a smaller diameter than the preceding monovalent ion. Sodium fluoride and magnesium oxide, for example, have exactly the same atomic arrangement, that of potassium chloride. The dimensions of the magnesium oxide structure are, however, smaller than those of sodium fluoride: the side of the unit cube is 4.22 \AA , as compared with 4.78 \AA . Since other data assign practically identical dimensions to oxygen and fluorine, the difference in the dimensions is accounted for by taking a smaller diameter for magnesium than for sodium. A comparison of the identical structures, magnesium carbonate and sodium nitrate, leads to the same result. We may ascribe this closer grouping of the atoms in the magnesium oxide or carbonate to the fact that the charges on the ions are double those in sodium fluoride or nitrate, so that the forces of attraction are more than four times as great. For the same reason the trivalent elements appear to occupy a still smaller domain in the crystal structure.

13. At the end of each period the diameters approach a lower limit. Since the electronegative elements are holding electrons in common, an estimate of the size of the outer electron shell can be formed from the distances which separate the atoms. The limiting values for the periods are, approximately :—

Neon	1.30 \AA
Argon	2.05 \AA
Krypton	2.35 \AA
Xenon	2.70 \AA

The diameters of the outer electron shells would appear to be equal to, or slightly less than, these values.

14. We can now review the types of crystalline structure. In what follows the various points have either been made by Langmuir or are direct consequences of the atomic theory which has been described above.

The crystals of a salt have been discussed above. Crystals of sodium chloride, or calcium carbonate, consist of ions of opposite signs. The ions are surrounded each by its own electron cloud ; they are held together by their electric charges, and kept apart by repulsive forces which must be supposed to exist between the outer electron shells. Diamond represents yet another type of crystal. The carbon atoms have each four electrons in the outer shell, and the complement of eight is attained by each carbon atom holding in common a pair of electrons with the four other atoms surrounding it symmetrically. The whole crystal is one molecule, all the atoms

being linked up by electron sharing, a view which is supported by the density and hardness of the diamond. A crystal such as quartz probably has the same type of structure. The structure of carborundum resembles very much that of diamond, and here again every atom shares electrons with all its neighbours.

The crystal of an electropositive element, such as lithium or potassium, has a different structure. Each atomic nucleus has a stable arrangement of electrons surrounding it, corresponding to one of the inert gases, and in addition one or more electrons must be associated with each atom according to its valency, as the whole mass of the metal is electrically neutral. The crystal may be regarded as composed of ions and electrons, the electrons having no definite place in the crystalline structure. If an electromotive force is applied to the metal they are driven through it; in other words, the metal is a conductor of electricity.

Still another type of association is that represented by water of crystallization, where some residual forces of attraction must be supposed to hold the electrically neutral water molecules in the crystalline structure.

15. Crystals where all the atoms hold electrons in common are characterized by great hardness; large forces are necessary to break the atoms apart. The typical salt, on the other hand, is soft, as in parting the atoms the only forces which have to be overcome are the electrostatic attractions between the atoms. An exception occurs when the ions have a double or treble charge and are close together, as in magnetite, Fe_3O_4 , and ruby, Al_2O_3 , for then the forces must be supposed to be so great as to give the crystalline structure considerable hardness.

In the crystal of a metal the ions, held together by electrons which probably have no fixed positions in the structure, are still freer to move past each other and give the metal its characteristic malleable and ductile properties.

Since the first two classes of crystals have no free electrons, they are non-conductors of electricity. This is the case for crystals of the electronegative elements where the atoms hold electrons in common. It is the last class of crystals, those of the electropositive elements, which are conductors.

16. In studying crystal structure we are studying the arrangement of the atoms in the solid state, for all true solids are crystalline in nature. It is the extremely short wave-length of the X-rays which makes this feasible. The limit to the minuteness of detail which it is possible to see under the microscope is fixed by the wave-length of the light used to illuminate the object, for it is impossible to distinguish two objects which are closer together than that wave-length. In the case of X-rays the wave-length is ten or twenty times smaller than the distances between the atoms, so that by illuminating the crystal with X-rays the atomic arrangement may be

analysed. It may be possible to push the analysis still further, and find in a direct manner the arrangement of the electrons around the nucleus. Experiments on these lines have already been carried out; for example, Debye's experiments on lithium fluoride.

17. I have tried to indicate the contribution which the study of crystals has made towards the solution of the problem of atomic structure, and the lines on which it may be expected to afford a still greater insight into that problem in the future. In considering the broadest aspects of the question it has been impossible to avoid generalizations to which many exceptions occur. I hope, however, to have shown that crystal structure has a wider significance than may perhaps be obvious at first sight. In a crystal the atoms and atomic groupings are ranged in perfect geometrical regularity, and it is by observing their concerted effects on the X-rays that we can investigate the intimate structure of solid bodies.

[W. L. B.]

Friday, February 11, 1921.

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Isotopes and Atomic Weights.

POSSIBLY the most important generalization in the whole history of chemistry is the Atomic Theory put forward by John Dalton in 1803, and it is a striking tribute to the shrewd intuition of that observer that of his five postulates only one seems to be in the least degree faulty, and over a century of active and unremitting investigation has been necessary to detect the flaw in that one.

The postulate in question states that "atoms of the same element are similar to one another and equal in weight." Of course, if we take this as a definition of the word "element," it becomes a truism; but, on the other hand, what Dalton meant by an element, and what we understand by the word to-day, is a substance such as hydrogen, oxygen, chlorine or lead, which has unique chemical properties and cannot be resolved into more elementary constituents by any known chemical process. For many of the well-known elements Dalton's postulate still appears to be strictly true, but for others—probably the majority—it needs some modification.

The general state of opinion at the end of the last century may be gathered from the following quotations from Sir William Ramsay's Address to the British Association at Toronto in 1897: "There have been almost innumerable attempts to reduce the differences between atomic weights to regularity by contriving some formula which will express the numbers which represent the weights with all their irregularities. Needless to say, such attempts have in no case been successful. Apparent success is always attained at the expense of accuracy, and the numbers reproduced are not those accepted as the true atomic weights. Such attempts, in my opinion, are futile. Still the human mind does not rest contented in merely chronicling such an irregularity; it strives to understand why such an irregularity should exist. . . . The idea . . . has been advanced by Prof. Schutzenberger, and later by Mr. Crookes, that what we term the

atomic weight of an element is a mean ; that when we say the atomic weight of oxygen is 16 we merely state that the average atomic weight is 16 ; and that it is not inconceivable that a certain number of molecules have a weight somewhat higher than 32, while a certain number have a lower weight."

That such conjectures were then regarded as wildly speculative shows how strong was the faith in Dalton's postulate, which is all the more remarkable when we consider that at that time not one single direct experimental proof of it had been offered. Such proof, obviously, can only be obtained by some method which measures the masses of atoms individually, and at that time none had been developed.

The first direct evidence that the atoms of an element were at least approximately equal in mass appears to be that obtained by Sir J. J. Thomson in 1910 by his well-known method of analysis of positive rays. The fact that sharply defined parabolic streaks were obtained at all proves that the ratio of the masses of the separate particles causing them to the charges of electricity they carry is constant. The latter was known to be a definite unit, or a simple multiple of it, so that if the masses of the individual atoms varied amongst each other in an arbitrary manner an indistinct blur would result instead of a clear-cut parabola.

Before going on to consider the evidence of positive rays in greater detail it will be as well to re-state briefly the evidence upon which the theory of isotopes was founded. The first indication that it might be possible to obtain substances having identical chemical properties but different atomic weights was afforded by the brilliant researches on the radioactive elements made by Sir E. Rutherford and his colleagues. Investigations on the transformations of the different radioactive families showed that certain products, such as lead, could be formed in several ways. Each of the leads so formed was found to have chemical properties identical in every respect with those of ordinary lead, but their method of production precluded any possibility of them all having the same atomic weight. Such bodies, although having different atomic weights, must occupy the same position in the Periodic Table of the elements, and on this account have been called "isotopes" by Prof. Soddy.

Moseley's epoch-making discovery has shown us that chemical properties depend not upon atomic weight but upon something much more fundamental, namely, *atomic number*. The atomic number of an element is the number of units of positive electric charge on the nucleus of its atoms ; the nuclear charge of hydrogen is 1, of helium 2, of lithium 3, and so on. We see, therefore, that isotopes are elements having the same atomic number but different atomic weights.

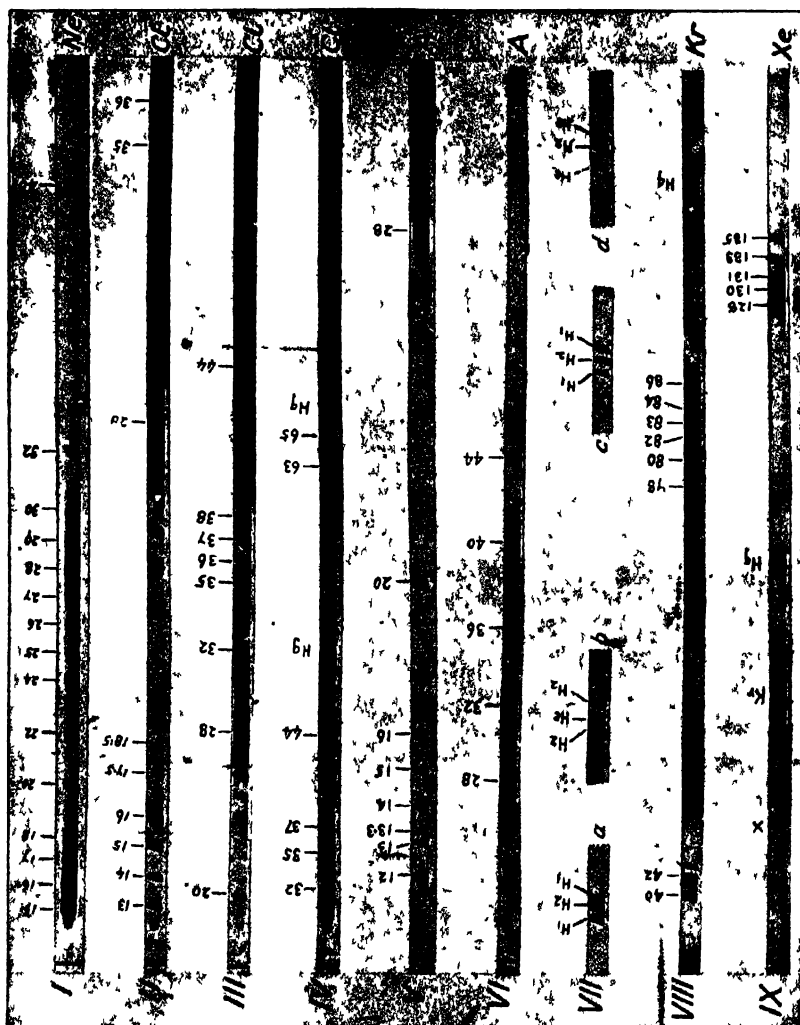
The theory of isotopes was triumphantly vindicated during the war by the researches of Soddy, Richards, Honigschmidt, and others, on the atomic weights of lead found in various radioactive minerals.

Quantities were obtainable which were ample for the most accurate determinations by chemical methods, and the atomic weights were found to differ from each other and from ordinary lead by quantities altogether outside possible experimental error.

Long before this convincing proof was forthcoming the theory of isotopes was discussed with the greatest interest in connection with atomic weights in general. If isotopes occurred among the heavy elements, why should they not be possible among the lighter non-radioactive ones? In which case elements with fractional atomic weights might clearly be mixtures, the constituents having atomic weights equal to whole numbers. This explanation was a very attractive one, for the curious jumble of whole numbers and fractions in the atomic weights when referred to oxygen as 16 has always been a serious stumbling-block in the way of any simple theory of atom building. The accurately determined atomic weight of chlorine 35.46 has certainly nothing to recommend it. It is reminiscent of the number of square yards in a square rod, pole or perch; but the idea of Nature, working on the same lines as the British weights and measures, is eminently unattractive.

The first support of the isotope theory among non-radioactive elements was given by the anomalous behaviour of the inactive gas neon when analyzed by Sir J. J. Thomson's method of positive rays. It is of interest to note that the announcement was made in this room by Prof. Thomson himself, and that the first sample of gas to show the effect was supplied by Prof. Sir James Dewar. This peculiarity was that whereas all elements previously examined gave single, or apparently single, parabolas, that given by neon was definitely double. The brighter curve corresponded roughly to an atomic weight of 20, the fainter companion to one of 22, the atomic weight of neon being 20.20. In consequence of reasoning adduced from the characteristics of the line 22, the discoverer was of the opinion that it could not be attributed to any compound, and that therefore it represented a hitherto unknown elementary constituent of neon. This agreed very well with the idea of isotopes which had just been promulgated, so that it was of great importance to investigate the point as fully as possible.

The first line of attack was an attempt at separation by repeated fractionation over charcoal cooled with liquid air, but even after many thousands of operations the result was entirely negative. It is some satisfaction to know that this result was inevitable, as Prof. Lindemann has recently shown, on thermodynamical grounds. Fractional diffusion through pipeclay was more effective and gave a positive result. An apparent difference of density of 0.7 per cent between the lightest and heaviest fractions was obtained after an exceedingly laborious set of operations. When the war interrupted the research, it might be said that several independent lines of reasoning pointed to the idea that neon was a mixture of isotopes,



angle θ is selected by the diaphragm D and passed between the circular poles of a powerful electromagnet O, the field of which is such as to bend the rays back again through an angle ϕ more than twice as great as θ . The result of this is that rays having a constant mass (or more correctly constant m/e) will converge to a focus F, and if a photographic plate is placed at GF as indicated, a *spectrum dependent on mass alone* will be obtained. On account of its analogy to optical apparatus, the instrument has been called a positive ray spectrograph and the spectrum produced a mass-spectrum.

Fig. 2 shows a number of typical mass-spectra obtained by this means. The numbers above the lines indicate the masses they correspond to on the scale $O=16$. It will be noticed that the displacement to the right with increasing mass is roughly linear. The measurements of mass made are not absolute, but relative to lines which correspond to known masses. Such lines due to hydrogen, carbon, oxygen and their compounds are generally present as impurities or purposely added, for pure gases are not suitable for the smooth working of the discharge tube. The two principal groups of these reference lines are the C_1 group due to C (12), CH (13), CH_2 (14), CH_3 (15), CH_4 or O (16), and the C_2 group (24 to 30) containing the very strong line C_2H_4 or CO (28). These groups will be seen in several of the spectra reproduced, and they give, with the CO_2 line (44), a very good scale of reference.

It must be remembered that the ratio of mass to charge is the real quantity measured by the position of the lines. Many of the particles are capable of carrying more than one charge. A particle carrying two charges will appear as having half its real mass, one carrying three charges as if its mass was one-third, and so on. Lines due to these are called lines of the second and third order. Lines of high order are particularly valuable in extending our scale of reference.

When neon was introduced into the apparatus four new lines made their appearance at 10, 11, 20 and 22. The first pair are second order lines and are fainter than the other two. All four are well placed for direct comparison with the standard lines, and a series of consistent measurements showed that to within about one part in a thousand the atomic weights of the isotopes composing neon are 20 and 22 respectively. Ten per cent of the latter would bring the mean atomic weight to the accepted value of 20.20, and the relative intensity of the lines agrees well with this proportion. The isotopic constitution of neon seems therefore settled beyond all doubt.

The element chlorine was naturally the next to be analyzed, and the explanation of its fractional atomic weight was obvious from the first plate taken. Its mass spectrum is characterized by four strong first order lines at 35, 36, 37, 38, with fainter ones at 39, 40. There is no sign whatever of any line at 35.46. The simplest explanation of

the group is to suppose that the lines 35 and 37 are due to the isotopic chlorines and lines 36 and 38 to their corresponding hydrochloric acids. The elementary nature of lines 35 and 37 is also indicated by the second order lines at 17.5, 18.5, and also, when phosgene was used, by the appearance of lines at 63, 65, due to COCl^{35} and COCl^{37} .

Quite recently it has been found possible to obtain the spectrum of negatively charged rays. These rays are formed by a normal positively charged ray picking up two electrons. On the negative spectrum of chlorine only two lines, 35 and 37, can be seen, so that the lines at 36 and 38 cannot be due to isotopes of the element. These results, taken with many others which cannot be stated here in detail, show that chlorine is a complex element, and that its principal isotopes are of atomic weight 35 and 37. There may be, in addition, a small proportion of a third of weight 39, but this is doubtful. Spectra I., II., III. and IV. show the results with chlorine taken with different magnetic field strengths.

The objection has been raised on many occasions that if chlorine consists of isotopes, how is it that its atomic weight has been determined so accurately and so consistently by different chemists? The obvious explanation of this appears to be that all the accurate determinations have been done with chlorine derived originally from the same source, the sea, which has been perfectly mixed for æons. If samples of the element are obtained from some other original source, it is quite possible that other values of atomic weight will be determined, exactly as in the case of lead.

The mass spectrum of argon shows an exceedingly bright line at 40, with second order line at 29, and third order line at $13\frac{1}{3}$. The last is particularly well placed between known reference lines, and its measurement showed that the triply-charged atom causing it had a mass 40 very exactly. Now the accepted atomic weight of argon is less than 40, so the presence of a lighter isotope was suggested. This was found at 36, and has now been fully substantiated; its presence to the extent of about 3 per cent is sufficient to account for the mean atomic weight obtained by density determinations.

The elements hydrogen and helium presented peculiar difficulties, as their lines were too far removed from the reference lines for direct comparison. By means of a special "bracketing" method moderately accurate values were obtained. Helium appears to be exactly 4 on the oxygen scale, but hydrogen is definitely greater than unity. The value obtained agrees very well with that already arrived at by chemical methods, namely, 1.008. At the same time, measurements of the 3 line, first observed by Sir J. J. Thomson, were made which came out at 3.024, satisfactorily proving it to be due to triatomic hydrogen.

Krypton and xenon gave surprisingly complex results, the former

consisting of six isotopes, 78, 80, 82, 84, 86. The weights of these could be determined with great accuracy by means of the excellent second and third order lines they gave. The first experiments with xenon lead to the observation of five isotopes, the provisional values of which were given as one unit too low. Owing to the kindness of Prof. Travers and Dr. Masson, I have recently been enabled to repeat the analysis with gas much richer in xenon. With this the second order lines could be observed and measured. The five principal isotopes of xenon are 129, 131, 132, 134, 136; there is apparently a faint sixth component at 128 and a doubtful seventh at 130.

Experiments with boron fluoride indicated that boron has at least two isotopes, 10 and 11, and that fluorine is a simple element of atomic weight 19.

Silicon is another unmistakably complex element having two isotopes, 28 and 29, with a possible additional one, 30.

Bromine was of great interest. As it has an atomic weight almost exactly 80, it might reasonably be expected to be simple and an isobare of one of the kryptons; actually it consists of equal parts of 79 and 81.

Sulphur, phosphorus and arsenic are all apparently simple elements. Mercury is certainly mixed, though its closer components cannot be resolved with the present apparatus. Its very characteristic groups are seen as high as the fifth order, and appear on nearly all the spectra taken. The group consists of a continuous succession of lines forming a band, 197 to 200, a strong line at 202, and a weak one at 204. Recently, at Copenhagen, Bronsted and Hevesy have succeeded in partially separating the isotopes of mercury by a fractional distillation at extremely low pressure. They give as their figures for the densities compared to normal mercury as unity—

Condensed mercury ...	0.999980
Residual mercury ...	1.000031

The error of experiment is claimed to be less than one part in a million.

Selenium, tellurium, antimony and tin have all been used in the discharge tube with no results of any value. This is unfortunate, for the atomic weight of selenium, 79.2, suggests that one of its isotopes must be an isobare of bromine or krypton; also the relation between tellurium and iodine is of great interest.

Iodine fortunately gave a very definite result. It is a simple element of atomic weight 127. This is rather surprising, for all the theoretical papers on the isotopic constitution of elements have predicted a complex iodine. Prophecy in physics becomes a difficult trade when experimental results produce these surprises, and apparently the only really reliable prediction is that there are plenty more in store for us.

The following is a list of elements and isotopes determined to date :—

TABLE OF ELEMENTS AND ISOTOPES.

Element	Atomic Number	Atomic Weight	Minimum Number of Isotopes	Masses of Isotopes in order of their intensity
H	1	1.008	1	1.008
He	2	3.99	1	4
B	5	10.90	2	11, 10
C	6	12.00	1	12
N	7	14.01	1	14
O	8	16.00	1	16
F	9	19.00	1	19
Ne	10	20.20	2	20, 22, (21)
Si	14	28.30	2	23, 29, (30)
P	15	31.04	1	31
S	16	32.06	1	32
Cl	17	35.46	2	35, 37, (39)
A	18	39.88	2	40, 36
As	33	74.96	1	75
Br	35	79.92	2	79, 81
Kr	36	82.92	6	84, 86, 82, 83, 80, 78
I	53	126.92	1	127
X	54	130.42	5, (7)	{ 129, 132, 131, 134, 136, (128, 130 ?)
Hg	80	200.60	(6)	(197, 200), 202, 204

(Numbers in brackets are provisional only)

By far the most important result of these measurements is that, with the exception of hydrogen, the weights of the atoms of all the elements measured, and therefore almost certainly of all elements, are whole numbers to the accuracy of experiment, namely, about one part in a thousand. Of course, the error expressed in fractions of a unit increases with the weight measured, but with the lighter elements the divergence from the whole-number rule is extremely small.

This enables the most sweeping simplifications to be made in our ideas of mass. The original hypothesis of Prout, put forward in 1815, that all atoms were themselves built of atoms of Protyle, a hypothetical element which he tried to identify with hydrogen, is now re-established, with the modification that the primordial atoms are of two kinds: atoms of positive and negative electricity.

Although the latter unit has long been known to us as an "Electron," its mate, which appears to be the real unit of mass, has only recently been given the name of "Proton."

The Rutherford atom, whether we take Bohr's or Langmuir's development of it, consists essentially of a positively charged central

nucleus around which are set planetary electrons at distances which are great compared with the dimensions of the nucleus itself. As has been stated, the chemical properties of an element depend solely on its atomic number, which is the charge on its nucleus expressed in terms of the unit charge e . A neutral atom of an element of atomic number N has a nucleus consisting of $K + N$ protons and K electrons, and around this nucleus are set N electrons. The weight of an electron on the scale we are using is 0.0005 , so that it may be neglected. The weight of this atom will therefore be $K + N$, so that if no restrictions are placed on the value of K any number of isotopes are possible.

The first restriction is that, excepting in the case of hydrogen, K can never be less than N , for the atomic weight of an element is always found to be equal to, or greater than, twice its atomic number. The upper values of K also seem to be limited, for, so far, no two isotopes of the same element have been found differing by more than 10 per cent of its mean atomic weight; the greatest numerical difference is eight units in the case of krypton. The actual occurrence of isotopes does not seem to follow any law at present obvious, though their number is probably limited by some condition of stability.

Protons and electrons may therefore be regarded as the bricks out of which atoms have been constructed. An atom of atomic weight m is turned into one of atomic weight $m + 1$ by the addition of a proton plus an electron. If both enter the nucleus the new element will be an isotope of the old one, for the nuclear charge has not been altered. On the other hand, if the proton alone enters the nucleus, and the electron remains outside, an element of next higher atomic number will be formed. If both these new configurations are possible they will represent elements of the same atomic weight, but with different chemical properties. Such elements are called "isobares," and are actually known among the radioactive elements.

The case of the element hydrogen is unique, for its atom appears to consist of a single proton as nucleus with one planetary electron. It is the only atom in which the nucleus is not composed of a number of protons and electrons packed exceedingly close together. Theory indicates that when such close packing takes place the effective mass will be reduced, so that when four protons are packed together with two electrons to form the helium nucleus, they will have a weight rather less than four times that of the hydrogen nucleus, which is actually the case.

It is not to be supposed that the whole-number rule is of exact mathematical accuracy, for the unit of the oxygen scale is a "packed" proton + an electron, and its value will certainly alter slightly with the degree of packing. On this account, it is of the greatest importance to push the accuracy of methods of atomic weighing as far as possible, for variations from the whole-number rule, if they could be

determined with precision, would give us some hope of laying bare that innermost of secrets, the actual configuration of the charges in the nucleus.

The results I have described lie on the border line of physics and chemistry, and, although as a chemist I view with some dismay the possibility of eighteen different mercuric chlorides, as a physicist it is a great relief to find that Nature employs at least approximately standard bricks in her operations of element building.

[F. W. A.]

Friday, April 22, 1921.

SIR JAMES REID, BART., G.C.V.O. K.C.B. M.D. LL.D. F.R.C.P.,
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SIR JAMES WALKER, D.Sc. LL.D. F.R.S., Professor of
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Electrosynthesis in Organic Chemistry.

[ABSTRACT.]

THE decomposition of water into oxygen and hydrogen by means of the electric current was effected by Nicholson and Carlisle in 1800, and affords the first example of electrolysis. Davy applied the electrolytic method to the decomposition of many compounds, and finally succeeded in isolating the alkali metals, potassium and sodium, by the electrolysis of fused potash and soda.

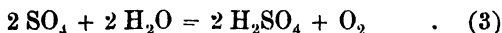
Faraday, his successor in the chair of the Royal Institution, laid the foundations of our theoretical knowledge of the subject. He studied in detail the nature and proportions of the products obtained by electrolysis, reduced the manifold experimental data to a simple system, and invented the nomenclature employed at the present day. The process of electrolysis in aqueous solution is conceived by him as follows: When two conducting plates connected with the opposite poles of a battery are immersed in a conducting solution, negative electricity travels towards the positive plate (*positive electrode, anode*), and positive electricity travels towards the negative plate (*negative electrode, cathode*). The electricity does not travel alone, but in association with a material carrier or *ion*, the *anion* or negatively charged ion moving towards the anode, whilst the *cation* or positively charged ion moves towards the cathode. Chemically equivalent quantities of the ions bear equal charges of electricity. When the ions reach the electrodes they are there discharged, and may then act (1) upon each other, (2) upon the water in which they are dissolved, or (3) upon the material of the electrodes. Thus, if we electrolyse sulphuric acid H_2SO_4 , which yields the ions 2H^+ and SO_4^{--} , we have at the negative electrode an action which may be represented by the equation



two discharged hydrogen ions combining with each other to form a molecule of hydrogen gas. If the positive electrode is of copper we have the reaction

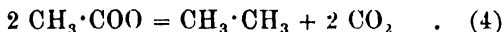


the discharged iron acting on the material of the electrode and forming copper sulphate. If, on the other hand, the positive electrode consists of the resistant metal platinum, the discharged ion acts on the solvent water according to the equation



sulphuric acid being regenerated and oxygen gas evolved.

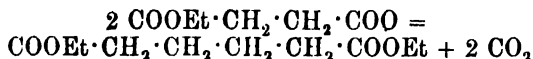
Equation (1) expresses a kind of synthesis, two atoms originally separate uniting to form a single molecule. In organic chemistry synthesis in the strict sense is held to mean the union of carbon atoms originally belonging to separate molecules. The first electro-synthesis was effected in 1849 by Kolbe, who, to take a simple example, electrolysed potassium acetate solution with platinum electrodes, and at the anode obtained the hydrocarbon ethane. The negative ion of the acetates is represented by the formula $\text{CH}_3 \cdot \text{COO}^-$, and under appropriate conditions two of these when discharged at the anode interact in accordance with the equation



Here an organic synthesis in the strict sense has been effected, two CH_3 groups originally contained in different molecules being now joined together by their carbon atoms to form a molecule of the hydrocarbon ethane $\text{CH}_3 \cdot \text{CH}_3$. This method of synthesis was for long neglected, but attention was again drawn to it in 1890 by a suggestion of Professor Crum Brown, which was worked out in detail in conjunction with the lecturer. If the sodium ethyl salt of a dibasic acid, e.g. malonic acid $\text{COOH} \cdot \text{CH}_2 \cdot \text{COOH}$, is electrolysed, the anion $\text{COOEt} \cdot \text{CH}_2 \cdot \text{COO}^-$ reacts according to equation (4) as follows:—



The product, diethyl succinate, contains two CH_2 groups instead of the single CH_2 group present in malonic acid, and may readily be converted into sodium ethyl succinate, which yields the anion $\text{COOEt} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COO}^-$. This on electrolysis reacts as before, thus:—



giving diethyl adipate, which now contains four CH_2 groups. This may be again converted into a sodium ethyl salt, and the process continued.

In this way it was possible to build up, starting from malonic acid, acids containing chains of 2, 4, 8 and 16 CH_2 groups. Starting from acids containing 3, 5 and 7 CH_2 groups, acids were prepared containing 6, 10 and 14 CH_2 groups, and with 6 CH_2 groups the acid with 12 CH_2 groups was prepared. Many acids with branched hydrocarbon chains have also been obtained by the method. In its simple form the electrosynthesis necessarily yields hydrocarbon chains with an even number of carbon atoms, a process of doubling taking place at each stage. However, acids containing an odd number of carbon atoms can be produced by the electrolysis of mixtures. Thus the acid containing 7 CH_2 groups has been prepared by the electrolysis of a mixture of the sodium ethyl salts of acids containing respectively 1 and 6 CH_2 groups, by the interaction of the two different discharged anions.

It is somewhat surprising that the method of electrosynthesis, an outline of which has been indicated, is not more extensively used in practice. Doubtless this is in part due to the care which must be exercised in adjusting the physical conditions in order to secure a successful result. Concentration of solution, temperature, material of electrode, electromotive force and current density at the anode all play an important part in determining the result of the electrolysis. Thus, for example, if we substitute a gold anode for a platinum anode in the electrolysis of a solution of potassium acetate, although the gold electrode is not attacked, and all other conditions remain the same, we obtain at the anode oxygen instead of a mixture of ethane and carbon dioxide. Here synthesis has not been effected: instead of the reaction of equation (1) it is now the action analogous to equation (3) which preponderates.

It is perhaps noteworthy that unlike many of the ordinary synthetic methods of organic chemistry which only succeed in unusual solvents or at comparatively high temperatures, the method of electrosynthesis yields the most successful results in aqueous solution and at the ordinary temperatures, resembling therein the synthetic processes which occur in plants and animals.

[J. W.]

Friday, May 27, 1921.

COLONEL E. H. GROVE-HILLS, C.M.G. D.Sc. F.R.S.,
Secretary and Vice-President, in the Chair.

A. MALLOCK, F.R.S.

Elasticity.

BEFORE speaking of the more special problems relating to elasticity, on which I have been recently engaged, it may be as well to define the meaning of the word "elasticity" in its scientific sense.

In ordinary conversation the terms "elastic" and "elasticity" have many different interpretations, but in physics it denotes simply a property possessed by all matter, but in various degree—namely, that of returning to its original form and dimensions after any cause which produces the alterations has ceased to act.

It has nothing to do with the hardness, softness, brittleness, or flexibility of the material. These are terms which depend on the limits of elasticity, and not on the elasticity itself. A billiard ball, for instance, is not by any means soft, but it is exceedingly elastic, as is shown by the absence of any permanent mark at the point where it has received the impacts of other balls.

The measure of elasticity is given by the force required to produce some known alteration of form, not exceeding in amount that which will naturally disappear when the force is removed.

Elasticity is of two fundamentally distinct kinds. All isotropic matter (i.e. matter which has the same properties in all directions), whether solid, liquid or gaseous, may be compressed bodily without change of shape, and it may also be distorted without change of volume. The forces which resist these alterations are known respectively as volume elasticity, or compressibility, and rigidity.

Any possible change of shape can be brought about by a suitable combination of volume compression (or dilation) and distortion (or "shear" as it is often called, from the identity of the action of distortion with the effect produced by a pair of shears).

Liquids and gases oppose hardly any resistance to distortion; in fact the mathematical definition of a "perfect fluid" is a material which offers no resistance whatever to distortion. Matter, however, in whatever state it may exist, resists compression, and in most cases this resistance is very large. Water, for instance, though its rigidity is nearly negligible, is only compressed by one three-hundred-

thousandth part of its volume by a pressure of 1 lb. per square inch, and for solids, such as metals, the compression would be much less.

The resistance to compression of fluids is easily shown, but the corresponding resistance to dilation, though it exists, is more troublesome to demonstrate by experiment, owing to the difficulty of securing the adhesion of the fluid to the surface of the vessel which contains it.

Experiments have been shown in this room in which water and mercury, free from air and placed in perfectly clean vessels, have borne large negative pressures, and the increment of volume which can be brought about in this way is limited by the want of adherence to boundaries rather than by the want of coherence in the liquids themselves. There is, however, a limit to the coherence of all liquid and solid matter when the volume is forcibly increased, and this limit is reached when the expansion is a very small fraction of the original volume.

In gases, on the other hand, there is no coherence, and the particles instead of holding together naturally tend to separate, a fact which is well accounted for by what is known as the molecular theory.

According to this theory, all the molecules of which the gas is made up are in continual motion, generally striking and rebounding from one another or from the boundaries which enclose them after a short free path. Pressure in a gas depends on the effect of the sum of these continual impacts, and thus not only on the velocity of the molecules, but also on the total number of molecules in a definite volume—that is, on the density. Temperature, on the other hand, depends on the average velocity only, the average velocity being taken as the square root of the mean of the squares of the velocities of all the molecules engaged. For air at ordinary temperatures and at atmospheric pressures this velocity is somewhat in excess of 1,600 feet per second.

The relation between pressure, volume and temperature to which the molecular theory leads is :

$\text{Pressure} \times \text{Volume} = \text{Absolute Temperature} \times \text{Constant},$

and this, taken as it stands, would indicate that if the temperatures were kept constant there would be no limit to the reduction of volume with the increase of pressure. The simple form of the theory takes no account of the size of the molecules themselves, and only represents the facts so long as the compression is insufficient to bring them into close contact with one another. When this contact does happen the variation of volume with pressure no longer depends on the reduction of the space between molecules, but on the compression of the actual molecules themselves, and there is every reason to believe that no force, however large, can reduce the volume of matter below a certain limit.

When the pressure is sufficiently increased and the temperature reduced, gases first liquefy and finally become solids, and so far as I know there have been no experimental determinations of the volume compressibility of liquid or solidified gases.

In fact singularly little is known as to the compressibility of any substance, even at the (what may be called) moderate pressure which can be produced in the laboratory. It is very difficult, for various reasons, to use pressure of 100 tons per square inch, which is very small compared to the pressure at the centre of the earth. By a well-known proposition it can be shown that if a certain mass is weighed at the earth's surface, and if the same mass were formed into a rod of uniform section and of the length of the earth's radius, and then lowered into a boring extending from the earth's surface to its centre, the gravitational attraction urging it downwards would be one-half of its surface weight.

The density of the earth is about 5.7, and the radius about 21 million feet. A rod one inch square, and of this density and length, would weigh just under 26 thousand tons at the earth's surface.

The pressure per square inch at the centre is therefore about 13,000 tons. At the centre of the sun the pressure would be more than thirty times as great.

Compared with this any experimental pressure seems insignificant.

The direct experiments on volume elasticity are chiefly on glass, water and mercury, in connection with the corrections for deep-sea thermometers, and also on certain other fluids, and the pressures employed range up to a few tons per square inch. (In Mr. C. A. Parsons' experiments on the compressibility of water the pressures were raised as high as 40 tons per square inch.)

I myself have made many trials of the compressibility of glass, indiarubber, various solid fats, and of minerals, such as asbestos, using pressures up to 24 tons. (These were in connection with the obturating pads used to make a gas-tight joint at the breech-blocks of large guns.) The method adopted in most of these experiments, including my own, depends on the measurement of the descent of a plunger under known loads into a strong vessel filled with the substance whose compressibility is to be found, and then applying corrections for the concomitant variation of the volume of the vessel, etc., induced by the applied pressure. It is in these corrections that the doubtful element appears in the results. For small pressures up to two tons per square inch I used a different procedure, in which the corrections were more easily dealt with. The matter for compression was placed in a glass cylinder, about ten inches high and three in diameter, the open end of which could be closed by a flat glass plate perforated with a small central hole.

A fine tube, connected with a small cistern of mercury, entered the vessel through this hole, and beneath it a second cup was

suspended to receive any mercury which might flow from the cistern. The matter to be tested was placed inside the cylinder, which was then completely filled with water, the cover was fitted on, and the whole placed in a strong steel explosion vessel also full of water, and the pressure was then pumped up as required. (Fig. 1.)

Thus there was practically no difference of pressure inside and outside the glass cylinder, and the volume of mercury which flowed through the tube (ascertained by weighing the contents of the cup) gave a measure of the volume compression of the contents of the former.

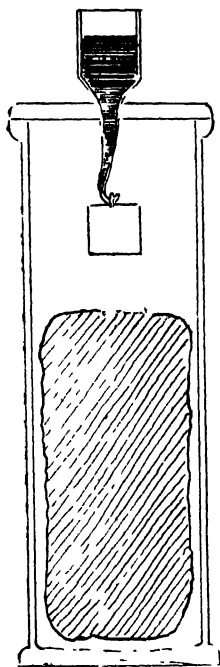


FIG. 1.

The only correction required is that for the volume compression of the glass and water, that for the small volume of mercury employed being negligible. The same method could probably be used with advantage at even the highest attainable pressures.

To sum up what is known as to the behaviour of matter when the volume pressure varies, it may be said that for any small change the variation of volume is directly proportional to the variations of pressure, and that while in the case of gases there is no limit to the possible expansion, no force, however large, can reduce the volume to less than the sum of the volumes of the molecules.

With liquids and solids there is a limit to the possible expansion, which is reached when the negative pressure exceeds the inter-molecular cohesion. When this limit is passed the extra space is either filled with the vapour of the substance, or is vacuous, and if the substance is a solid fracture occurs.

For a substance which has the same properties in all directions volume compression cannot cause rupture, and a cube, for instance, would remain a cube, no matter how much it was compressed, the only change being in the absolute dimension.

For crystals or other substances which have different compressibilities in different directions this is not so obvious, and it is not known whether the different elastic properties of crystals in the principal axes depend on compressibility or on rigidity, or both.

Rigidity, or resistance to change of shape, has been more fully investigated, experimentally at any rate, than compressibility.

What happens during distortion can be illustrated by supposing that two opposite faces of a cube are fixed to two parallel planes, and that these are forced to slide while remaining parallel and at a

constant distance from one another. It is evident that the volume of the cube is unchanged by this process, but the lengths of the diagonals of two of the faces are changed, one being shortened and the other lengthened.

If a square be inscribed on one of the faces before distortion with its edges parallel to the diagonals, the subsequent distortion changes it to a rectangle whose length is $1 + e$ and breadth $1 - e$. If F is the force required to produce the alteration, the rigidity is defined by the relation $F = ne$, or the coefficient of rigidity, n , is equal to F/e , and is the force which if applied as a pull over one pair of opposite faces of a cube and a push over another opposite pair would (if strain and stress remained directly proportioned to one another) double its length.

In ordinary solids strain and stress are only proportional within generally rather narrow limits, which, however, vary widely in different materials, as, for instance, in glass compared with india-rubber.

When these limits are exceeded the material is either ruptured or permanently distorted.

The point to which attention should be directed is that the limits for rigidity are quite different and apparently independent of those for dilatation.

As has been said before, volume elasticity and rigidity are the fundamental qualities which regulate the elastic behaviour of a solid, but the quality most ordinarily in evidence is the elastic resistance opposed to a direct pull.

This is known as Young's Modulus, and may be defined as the direct pull which would be required to double the length of a rod of uniform section, assuming strain and stress to be always proportional. If the modulus is denoted by E , and an extension e is caused by a direct pull F ,

$$E = F/e.$$

E differs from the rigidity constant n in that no force is applied at right angles to the pull, and it involves the volume elasticity k , as may be shown by the diagram (practically the same as that given in Thomson and Tait's "Natural Philosophy") in slide (3). Let the direct pull at the two opposite faces of the cube be represented by P , and let P be divided into three equal parts as shown. On the other four faces of the cube let forces each equal to $\frac{1}{3} P$ act in opposite directions.

The joint action of all these forces is a direct pull equal to P tending to increase the distance between the first-named pair of faces, while no force is exerted on the other two pairs. This is equivalent to two shearing stresses at right angles to one another, each equal to $\frac{1}{3} P$, combined with dilating stress equal to $\frac{1}{3} P$ in all directions.

The extension due to the two shearing stresses is therefore

$$P \left(\frac{2}{3n} + \frac{1}{9}k \right),$$

and hence

$$\text{Young's Modulus (E)} = \frac{9nk}{3k+n}.$$

Although no force is exerted on the lateral face this does not imply that there is no change of lateral dimensions, for the contraction due to the shearing stress is $\frac{P}{6n}$ in both lateral directions, while the dilatation in the same direction is only $\frac{P}{9k}$.

If the extension due to a direct pull is compared with the consequent change of diameter, it will be found that

$$\frac{\text{Lateral contraction}}{\text{Longitudinal extension}} = \frac{1}{2} \frac{3k-2n}{3k+n}.$$

This ratio, generally denoted as μ , plays an important part in many physical and mechanical problems. It is known, rather ironically, as "Poisson's Ratio"—Poisson having proved, as he thought, that the ratio was the same for all solids, and equal to one-quarter.

As a matter of fact it may have any value between $\frac{1}{2}$ and 0, according to the relative magnitudes of the volume elasticity and the rigidity.

If a solid is easily distorted but offers great resistance to compression, the sides move out or in by almost half the distance by which the ends are moved in or out, and if the rigidity is great compared to the volume compressibility, the reduction or increase of length makes hardly any difference in the diameter.

This may be shown by a simple experiment. I have here a cylinder of indiarubber and a cylinder of cork, placed between two washers on steel bolts. Indiarubber is a substance which can be easily distorted, but offers great resistance to volume compression. Cork, on the other hand, resists distortion much more than it does volume compression. It will be seen, when both are reduced to about half their original length by turning the nut on the bolt, that the diameter of the indiarubber has increased by nearly one-quarter, while that of the cork has hardly changed.

The whole of the mathematical theory of Elasticity turns on the four quantities k , n , E and μ , together with the assumption that these are constants for the range of strains and stresses contemplated in the problems.

As before mentioned, there has been very little direct experimental work on volume compressibility, but if Young's Modulus

and the rigidity coefficient are known (and both are easily determined), the volume compressibility can be deduced from the relation (derived from the expression for E in terms of k and n)—

$$k = \frac{1}{3} \frac{E n}{n - E}.$$

All, or nearly all, the values of the coefficient of volume compression given in books of reference or in table of constants are reached in this way.

But k may also be found if the values of Poisson's and the rigidity are known, for from the expression for μ it will be seen that

$$k = \frac{2 n}{3} \frac{(1 + \mu)}{(1 - 2 \mu)}.$$

Poisson's Ratio is not perhaps as easily determined by direct experiment as Young's Modulus or the rigidity coefficient. In 1877, however, I employed a method which was applicable to most materials and was susceptible of considerable accuracy. This I will shortly describe and illustrate the procedure by a model.

When a flat bar is bent the material on the convex side of the neutral plane is stretched in the direction of the length and compressed on the concave side, with the result that diameter of the bar is reduced on convex face and increased on the concave. In consequence the cross-section of the bent bar is no longer rectangular, but has its faces curved in the opposite sense to the curvature of the longitudinal section. It is easy to see that the ratio of the two principal radii of curvature depends on the ratio of lateral contraction to longitudinal extension, and that if this ratio of the curvatures can be measured the value of μ for the material of the bar can be deduced.

In my own experiments the bar was bent by equal couples applied at the end; thus the bar originally straight became an arc of a circle. On the middle part of the surface a circle was described whose diameter was a little less than that of the bar itself, and at the ends of the diameters of this circle, parallel and perpendicular to the length of a bar, four fine steel wires were planted forming normals to the unstrained surface. The wires remain normal to the surface from which they spring when the bar is strained. Hence the free ends of the pair on the longitudinal diameter move apart when the bending couple is applied, while those on the transverse diameter approach one another. (See Fig. 2.)

The distances through which they moved were measured with a microscope and micrometer, and a comparison of the displacements of each pair gave the data for the calculation of μ .

The elastic properties of matter vary with the temperature, and during the last few years I have examined the changes which occur

in various metals and a few non-metallic substances from this cause. The range of temperature covered by the experiments lay between 100°C . and the temperature of liquid air. I had hoped to go as low as liquid hydrogen temperatures, but the difficulty of getting a sufficient supply of the liquid has been in the way.

The first series of experiments were on the temperature change of Young's Modulus, and the slide (6) will show the form of apparatus adopted for the purpose.

It was necessary to be able to work on small test-pieces, both on

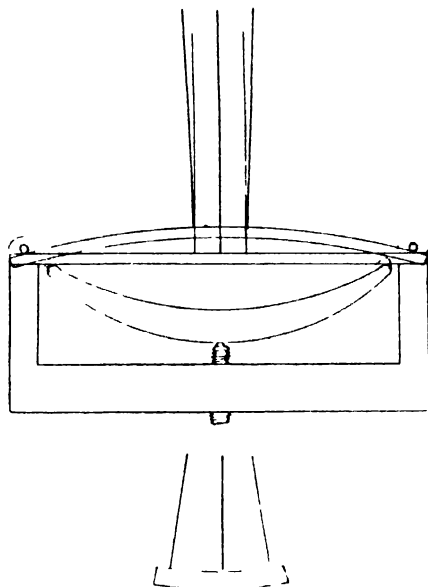


FIG. 2.

account of cost of such metals as rhodium, platinum, etc., and of the convenience of having a moderate-sized lathe for the heating or cooling liquids.

Four temperatures were generally tried for each test-piece—viz. 100°C ., ordinary temperature about 14°C ., a freezing mixture of alcohol and carbonic acid (-100°C .), and liquid air (-173°C .).

The test-pieces were in the form of thin plates an inch and a half long and about a quarter of an inch wide, with a thickness of one or two hundredths of an inch. The lower end of the test-piece was

clamped to a fixed support carried on a stout glass rod. The upper end was clamped to a stiff hardwood rod, wood and glass being chosen as being bad conductors of heat.

Mounted in this way the rod could oscillate (like one end of a tuning-fork), and being itself so stiff compared to the test-piece as to remain practically unbent, the force of restitution was determined by the elasticity and dimensions of the test-pieces only. The elastic quality called into play when a bar or plate is bent is Young's Modulus, and hence to determine the variations of Young's Modulus at different temperatures it was only necessary to compare the periods of oscillation of the test-piece at those temperatures, the temperature being the only condition which was altered (if the small correction due to dilatation or contraction is neglected). The actual dimensions of the test-piece and the periods do not matter, all that is required being the comparison of its periods at different temperatures. In order to make this comparison the actual periods had to be measured with considerable accuracy.

The periods employed were generally between half a second and two seconds, and if the rod is displaced and then left to itself the oscillations so started would from various causes die out before a sufficient number could be counted to give an accurate result—accurate, that is, to one part in two or three thousand. The oscillations therefore were maintained by an arrangement I had before used for an electric clock. This gave an impulse to the rod at the moment of its passing through the zero position. An impulse given to an oscillation at that time has no effect on the period, but merely increases its amplitude if there is no resistance, or if there is resistance keeps the amplitude constant by adding at each impulse the loss sustained during the previous beat.

It is shown in the slide (7). (Description.)

I have the maintainer here, but as its action could not be well shown when applied to experiments described, I have arranged it to maintain the vibrations of a pendulum the image of which will be thrown on the screen.

The current which worked the magnets of the maintainer was also used to record each oscillation on a chronograph on which a clock recorded seconds of time. In this way time could be measured to about $\frac{1}{30}$ th of a second, and since from 100 to 300 or more oscillations were generally made by the rod in each experiment, the period could be well determined.

It was observed that the more fusible was the metal subjected to trial the greater was the variation of the elasticity with change of temperature, the change being always an increase of the value of Young's Modulus with a decrease of temperature.

The metals tested were (in the order of their melting point), rhodium, platinum, iron, palladium, nickel, copper, gold, silver, magnesium, aluminium, zinc, lead, cadmium, bismuth, and tin.

If the variations of Young's Modulus depended solely on the melting point, the assumption might be stated in the form—

Young's Modulus at temperature θ_1 absolute is to that at θ_2 as θ_1 is to θ_2 , so that if $\theta_1 = 0^\circ \text{C.}$ and $\theta_2 = -273$

$$\frac{E \text{ at } 0^\circ \text{C.}}{E - 273^\circ \text{C.}} = \frac{\text{Melting point Centigrade}}{\text{Melting point Centigrade} + 273^\circ \text{C.}}$$

In the full curve represented in the slide (8) the ordinates give the variations of Young's Modulus for a metal whose melting point (absolute) is indicated by the abscissa, calculated from the equation. (Fig. 3.)

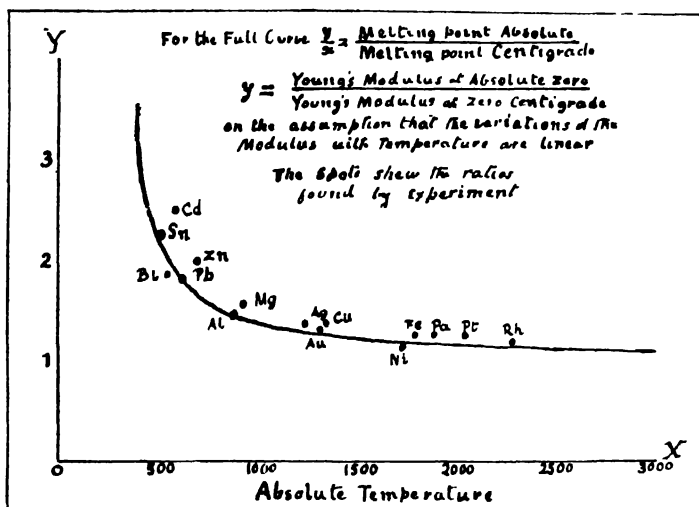


FIG. 3.

The circles show the variations actually found for the various metals above-mentioned, and though it is evident that something beside the melting point influences these results, the experimental points do show a tendency to follow the curve, though the variations found by trial are generally in excess of those estimated.

Young's Modulus being a complex quantity, depending both on rigidity and compressibility, I thought it would be of interest to try experiments in which rigidity only was involved, and this was done by timing the torsional vibrations of test-pieces in the form of wires or very narrow strips of plate.

The apparatus used is shown in the slide (9). A vertical rod suspended by a long fine wire carries a cross-arm weighted at both ends, to increase its moment of inertia; the test-piece is clamped to

Two methods of arriving at the desired information have been tried.

The first is to record not only the periods, but also the amplitudes of the free oscillations. In this method the oscillation is not maintained, and the rate at which the motion dies out gives a measure of the work lost at each instant.

The second plan is to maintain a forced oscillation of constant amplitude by the application of a known harmonic couple, and to record the amplitude of the forced oscillation and the relation between phases of this and of the maintaining couple. When these elements are known it is a simple matter to calculate the work expended in maintaining the constant amplitude.

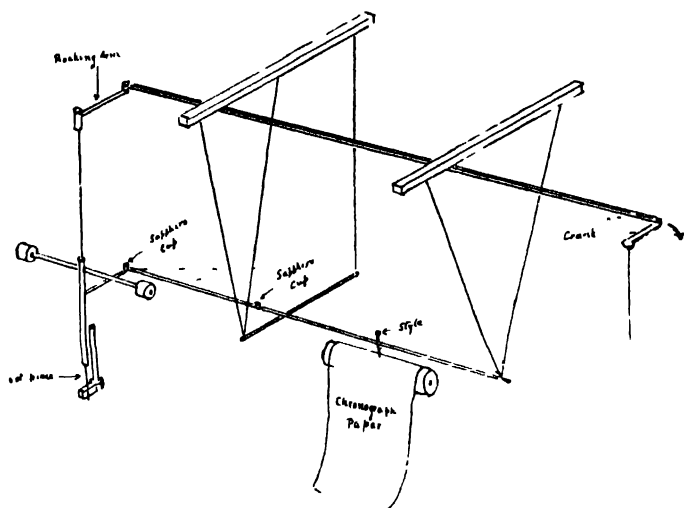


FIG. 5.

In experiments such as these, where the object is to record resistance, great care is required to exclude all sources of resistance other than that which is to be measured, and in particular to eliminate all chance of solid friction. Viscous resistance in the recording mechanism when small can be determined by separate experiments and its effects allowed for.

The apparatus employed is on the lecture table, and as far as the oscillating parts are concerned is the same as that used in the previous series, except that provision is made for the application of a forcing couple to the suspension wire, and a light horizontal arm is added to the suspended rod, from the end of which arm a connecting rod transmits the motion to the style recording the amplitudes on the

chronograph. It is in these parts that constant friction is most likely to occur.

The slide (10) shows the general arrangement. The style is mounted on a horizontal reed so hung by silk fibres as to have only one degree of freedom—namely, that of motion parallel to its length, and at right angles to the travels of the chronograph paper. (Fig. 5.) This kind of suspension I have used on a larger scale for ballistic pendulums.

I chose a reed (*Arundo phragmites*) as a style-carrier on account of its lightness and rigidity. Such reeds are practically wooden tubes with walls less than a hundredth of an inch thick, coated with a stiffening layer of silica.

One end of the reed is terminated by a fine vertical steel point, as also is the end of the horizontal arm on the oscillating rod. The connecting rod which joins the two is also a reed, at either end of which are mounted sapphire cups such as are used for magnetic compasses.

It was essential that the style should not touch the paper on which it recorded its position, and this condition I at first intended to satisfy by using a syphon-recorder of Sir W. Thomson's type. I found, however, that it was much simpler to use an ordinary induction coil, the sparks from which, if properly adjusted, left an excellent trace on the moving paper. The style, therefore, took the form of a steel needle passed through the reed with its point about a hundredth of an inch above the surface of the chronograph paper.

One of the records obtained in this way is now shown as a lantern slide. (See Fig. 6.)

This exhibits the rapid natural extinction of the oscillation in the metal tin.

In order to apply a known harmonic forcing couple to the oscillating parts a horizontal arm was fixed to the upper end of the suspension wire, and this, by a long connecting rod working from a crank of adjustable throw, was made to twist the wire harmonically through any desired angle.

The crank was driven by a small electro-motor through a reduction gear, and its speed regulated by the position given to a belt on two cones, one cone being driven by the motor, and the other, by a second belt, driving the crank shaft.

The motor itself was controlled by a centrifugal governor, which regulated the current supplied to it from the main. Each revolution of the crank shaft was recorded on the chronograph, so that the relative phases of the applied couple and the forced oscillation could be compared.

The experiments depending on oscillations have not yet been completed, but the next three slides show some of the results obtained by the experiments on the extinction of the natural oscillations.

In slide (12) these are put in the same form as in (8), and they

indicate that rigidity-variation depends on the temperature of the melting points very nearly in the same way as does Young's Modulus. (Fig. 7.)

In the next slides (13 and 14) are shown the percentage variation of rigidity of the various metals between the limits of the temperatures employed in 100°C. to -176° . It will be seen that the increase in rigidity as the temperature falls is not linear, and that there is not sufficient evidence to make even a useful guess at what the rigidity would be at absolute zero.

In slides (15 and 16) are shown the variations of viscosity for same selection of metals.

To explain these diagrams it may be stated that the oscillations

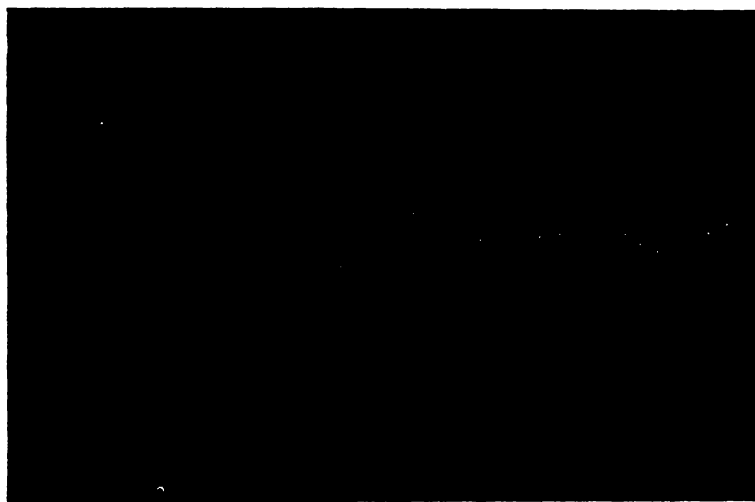


FIG. 6.

of viscous substances, where the strain does not exceed the limits of elasticity, naturally decrease at compound interest—that is, the amplitude of each successive oscillation is some constant fraction of the one which preceded it. In symbols, if A_0 is the amplitude at time t_0 and A_t the amplitude at time t , then

$$A_t = A_0 e^{-\frac{t-t_0}{c}},$$

where c is a constant, and this constant is the time in which the amplitude is reduced in the ratio of e to unity.

The ordinates of the curve shown in the slide are the proportional times in which the viscosity of the metals causes a reduction of $e : 1$

at the temperature indicated by the abscissa, the time at 100°C . being taken as unity.

Although on the whole the metals become less viscous at low temperatures, there seems to be an actual increase, or slower rate of decrease, of viscosity somewhere between 0° and -100°C ., which is particularly noticeable in the case of copper, gold and silver.

This is a matter which requires further investigation. The same metal often gave different results in the annealed and hard conditions.

There is no very apparent connection between the variations of viscosity and the melting points, although the easily fusible metals show the larger changes in this respect.

A general conclusion which I think may be drawn from these

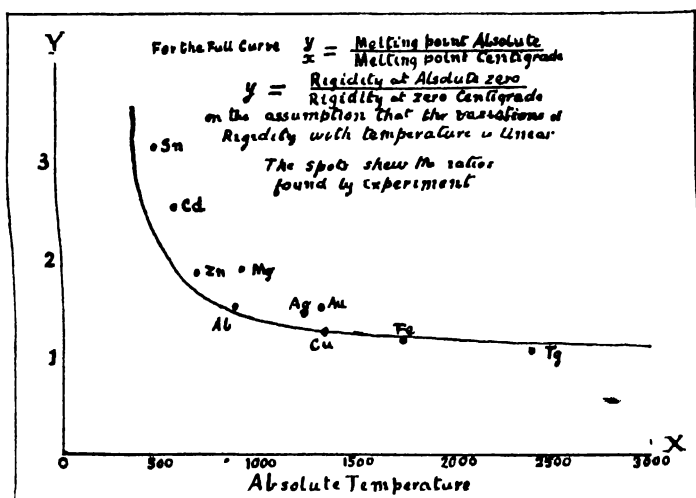


FIG. 7.

and the former experiments is that the rigidity of any metal and its variation with temperature is not much affected by the present state of the test-piece or its previous history, being nearly the same for hard, soft, cast, forged or annealed specimens; but that the viscosity, both as regards its absolute value as well as its temperature variations, is influenced by all these conditions, though not so much as are the elastic limits.

I have here an experiment which will show how small is the difference between the elasticities of hard and soft steel, and between these and wrought iron.

A bar of hard steel is laid horizontally on supports at either end. A weight can be hung from the centre and will cause a certain deflection, indicated on an enlarged scale by the pointer. On sub-

stituting a bar of the same dimensions, but well annealed, it will be seen that the same deflection is shown. Using a similar bar of wrought iron, the deflection is only a little greater.

The limits of elasticity are of course widely different in all three cases.

In engineering and structural work it is the limits of elasticity which are important to designers rather than the elasticity itself, for it is on these limits that the strength of materials depends. The elasticity enters into calculations of the reaction of springs, in which is included the deflection of loaded structures, such as girders and bridges; for all structures, whether meant to be rigid or not, are in effect springs with longer or shorter periods of vibration. It is the strain limits, however, of the materials, and not their elasticities, which decide what loads can be safely borne.

When a material is strained beyond its elastic limits it either takes a permanent set or is ruptured, and the manner in which set or rupture occurs gives rise to such qualifications as hard, soft, brittle, tough, malleable, ductile, friable, plastic, etc.

The behaviour indicated by these adjectives can be explained by the relative differences between the volume elasticity and rigidity in conjunction with the limits of strain which either kind of elasticity will withstand.

When a substance is said to be hard or soft (in the metallurgist's sense) it is implied that the rigidity is great or small. For the mineralogist hardness has another meaning, and refers to the properties of a surface as opposed to that of a volume. If one material will scratch another, the one which is scratched is considered the softer of the two, and by this test a rough and arbitrary scale of mineralogical hardness has been established, ranging from diamond at one end to talc at the other.

I believe that this sort of surface hardness is analogous to surface tension, for it is hardly to be thought that the causes which produce surface tension in fluids cease to operate in the case of solids. On this view hardness of this sort might be defined as the limit of tangential strain at a surface which can be borne without rupture. This may be very different from the strains which can be borne in the interior. For example, diamond is the hardest substance known in the mineralogical sense, but it can be easily crushed by hard steel, showing that one, at any rate, of the strain limits for diamond is less than it is for steel.

A body is brittle if, whether hard or soft, the limits both for volume extension and rigidity are small, and the characters of the fractured surface will often help to determine which of these limits is the greater; but it would take too long to enter into the details of the subject at this time.

Malleability implies that the material can be worked without rupture under the hammer; ductibility, that it can be drawn out

into wire or tube. The stresses produced by hammering are shear and volume compression, while in drawing they are shear and volume extension.

Hence it may be concluded that in a material which is malleable but not ductile, the limit of strain for volume expansion is less than the rigidity limit, and also, that body which is ductile is also malleable, but that the converse is not true.

Plastic bodies are those which when distorted do not rupture but retain their distorted shapes, and this implies that the elastic limits for rigidity are small, but that the limit for permanent set are large.

I will conclude by showing a few experiments designed to illustrate fracture by volume extension and fracture by shear.

I have here some brass rings over which damp paper has been stretched. The contraction of this paper as it is dried by the heat of the lantern will be sufficient to cause rupture.

In the stress due to contraction volume extension is predominant in the proportion of two to one.

It is impossible to foretell in what position or direction the break will occur. In an isotropic material this would be a matter of pure chance, but in the present case some irregularity in cementing the paper to the ring or in the structure of the paper itself will decide.

In the next experiment a sheet of brittle material will be broken by shear. The material used is a square of dried sheet gelatine, two of whose opposite edges are gripped by clamps, which are then made to slide parallel to one another at a constant distance.

If the sheet were thick enough to withstand edgeway pressure without folding, the applied stress would be a simple shear, and in the actual case shear is predominant. The direction of the fracture, as will be seen, is nearly at right angles to the extended diagonal.

Lastly, I will break some of the same gelatine which has had its limits of shear increased by the absorption of water, and draw your attention to the shape of the termination of the cracks which have been started.

At the end of a spreading crack the material is undergoing intense distortion, and when the limit for shear strain is much in excess of the volume strain limit, the termination of the crack is, as in the present instance, rounded.

In a note appended to this lecture the effect of the relative magnitude of the elastic constants and their limits on the character of permanent set and fracture is considered in somewhat greater detail. The subject is one on which much useful work might be done.

In conclusion, I wish to give my best thanks to the Director of the Davy Faraday Laboratory, where the greater part of the experiments on Rigidity have been carried out. The experiments, in fact, could not have been made without the facilities for dealing with low temperatures which the Davy Faraday Laboratory has afforded.

[A. M.]

Friday, June 10, 1921.

SIR JAMES REID, Bart., G.C.V.O. K.C.B. M.D. LL.D.,
Vice-President, in the Chair.

ARTHUR GORDON WEBSTER, D.Sc. LL.D. Hon.M.R.I.,
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Absolute Measurements of Sound.

It is now more than thirty years since it occurred to me to devise an instrument that should be capable of measuring the intensity or loudness of any sound at any point in space, should be self-contained and portable... and should give its indications in absolute measure. By this is meant that the units should be such as do not depend on time, place, or the instrument, so that, though the instrument be destroyed and the observer dead, if his writings were preserved another instrument could be constructed from the specifications and the same sound reproduced a hundred or a thousand years later. The difficulty comes from the fact that the forces and amounts of energy involved in connection even with very loud sounds are extremely small, as may be gathered from the statement that it would take approximately ten million cornets playing *fortissimo* to emit one horse-power of sound.

Before we can measure anything we must have a constant standard. In sound we must construct a standard which emits a sound of the simplest possible character, which we call a pure tone; it will be like that emitted under proper conditions by a tuning-fork, which is described by saying that the graph representing the change of pressure with the time shall be that simple curve known as the sinusoid or curve of sines. From this connection we say that the pressure is a harmonic function of the time. Unfortunately, the pressure change is so small that at no point in a room, even when a person is speaking in a loud tone, does the pressure vary from the atmospheric pressure by more than a few millionths of an atmosphere. Thus we require a manometer millions of times as sensitive as an ordinary barometer, and, in addition, since the rhythmic changes occur, not once in an hour or day, but hundreds of times per second, if we wish the gauge to follow the rapid changes accurately, we have many mechanical difficulties.

The problem of a standard of emission has been solved by a

number of persons, including Prof. Ernst Mach and Prof. Ludwig Boltzmann, and Dr. A. Zernov, of Petrograd, a pupil of the celebrated Peter Lebedeff. The problem of an absolute instrument for the reception and measurement of a pure tone has been also successfully dealt with by a number of investigators, among whom may be mentioned Prof. Max Wien, of wireless fame, the late Lord Rayleigh, and Lebedeff. But there remains a third step in the process, which is as important as the first and second. Given the invention of the proper standard source of sound, which I have named the "phone," because it is *vox et præterea nihil*, and of a proper measuring instrument, which should evidently be called a phonometer, there still remains the question of the distribution of the sound in space between the phone and the phonometer. Any measurements made in an enclosed space will be influenced by reflections from the walls, and, even if we had a room of perfectly simple geometrical form, say cubical, and were able to make the instruments of emission and reception work automatically without the disturbing presence of an observer, it would still be impossible to specify the reflecting power of the walls without a great amount of experimentation and complicated theory. Nevertheless, this is exactly what was done by the late Prof. Wallace C. Sabine, of Harvard University, who employed the human ear as the receiving instrument. Those who have made experiments upon the sensitiveness of the human ear for a standard sound will immediately doubt the possibility of making precise measurements by the same ear at different times, and particularly of comparing measurements made by one ear with those made by another. Nevertheless, Sabine attained wonderful success, and was able to impart his method to pupils who carried on his work successfully, so that he was able to create the science of architectural acoustics and to introduce a new profession. Still, the skill that required three or four months to attain 'by Sabine's method may be replaced by a few minutes' work with the phonometer.

In order to avoid the influence of disturbing objects, the observer should take the phonometer to an infinite distance, which is manifestly impossible. The method employed was to get rid of all objects except a reflecting plane covered with a surface the coefficient of reflection of which could be measured. For this purpose the teeing ground of a suitable golf course was used. With the present instrument it can be determined in a few minutes, if there is no wind.

In 1890 I proposed to use a diaphragm made of paper, which should be placed, shielded on one side, at the point where the sound was to be measured. In order that the effect of the sound should not be distorted, the membrane, instead of having to do any work, as in the case of the diaphragm of the phonograph in digging up the wax, or in that of the microphone in compressing the carbon, was to be perfectly free, but was to carry a small plane mirror cemented on at its centre. In close juxtaposition and parallel with this was the

plane side of a lens which, viewed in the light from a sodium flame, was to give Newton's rings or interference fringes. Of course, when the sound falls upon the diaphragm the fringes vibrate rapidly and disappear from sight.

By the introduction of a Michelson optical interferometer, two of the difficulties of this instrument were overcome—namely, (1) that of adjusting the lens so that it would not strike the vibrating mirror, since the mirrors in the interferometer could be as far apart as one pleased; and (2), more important still, it permitted the use of fringes in white light, so that it was possible to use gas, incandescent, or arc light with excellent effect. A further improvement was introduced by the use of a thin plate of mica for the diaphragm.

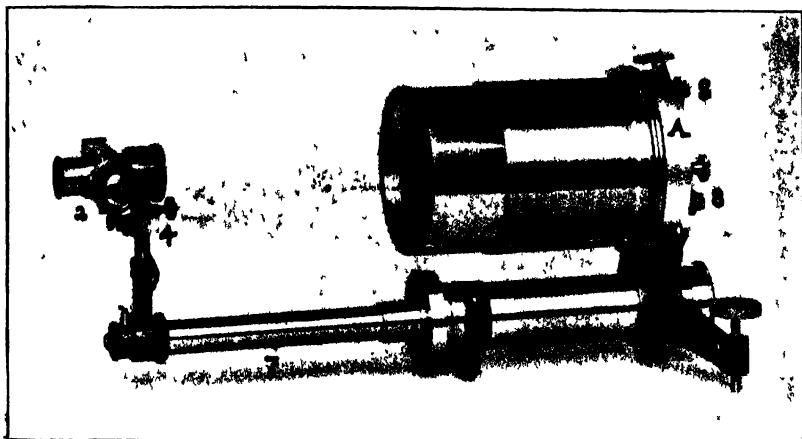


FIG. 1—PHONOMETER. (Interferometer not shown)

To obtain the sensitiveness necessary to measure sounds of ordinary intensity, the property of resonance is employed twice—i.e. a system of two degrees of freedom is used. First, the plate resonates to a sound more strongly as it is tuned more nearly to it; and second, a resonator that can also be tuned is put behind the plate. The sound entering by the hole in the resonator is magnified by the tuning, and acts upon the plate, which is also tuned. A graph can be plotted in which one co-ordinate represents the stiffness of the plate, or rather what may be called the mistuning, which is the stiffness lessened by the product of the mass by the square of the frequency. The other co-ordinate represents the corresponding quantity for the resonator, the stiffness of which depends simply on the volume into which the air is compressed, while the effective mass depends on the dimensions of the whole, and its damping on the sound radiated from the mouth. It is then found that the tuning

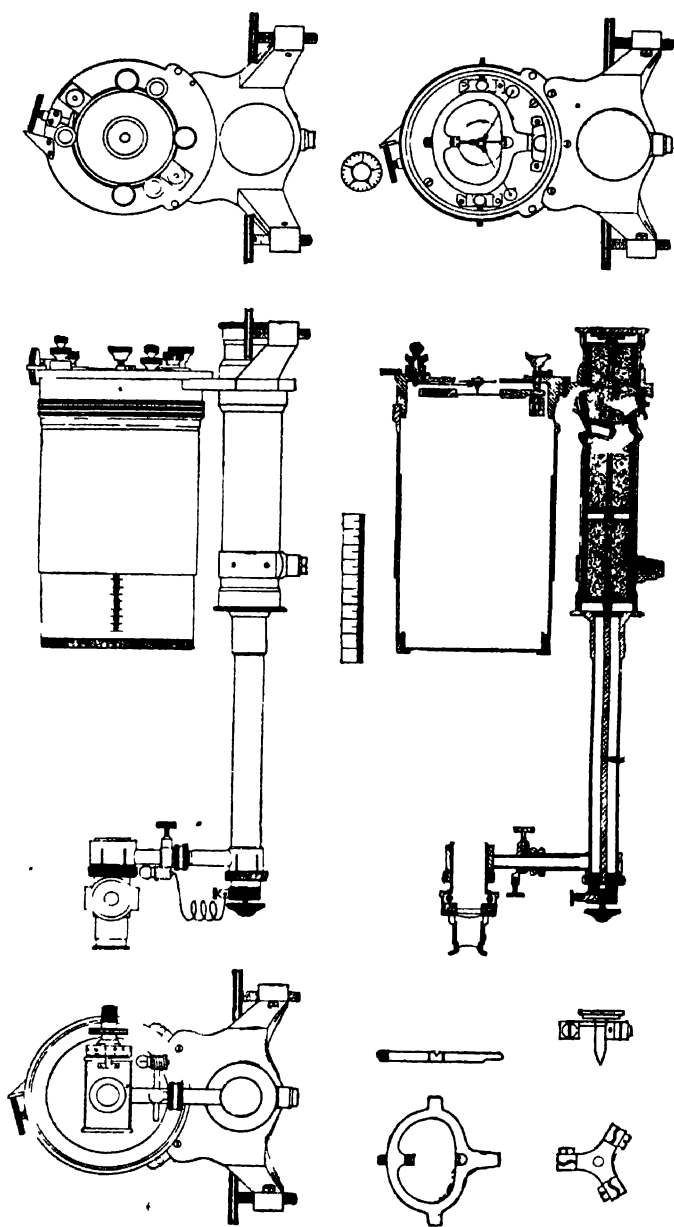


FIG. 2.—PARTS OF THE PHONOMETR.

should not be such as to make the representative point occur at the middle of the figure, making both mistunings zero, but that both mistunings should be of the same sign and a certain magnitude, depending on the coefficients of damping of the two degrees of freedom of the coupled system. The mathematical theory is precisely that of a wireless receiver. The ultimate sensitiveness depends on the smallness of the damping of the plate.

The apparatus as it was built several years ago was mounted upon a heavy bronze stand, covered at the back by a heavy bronze cover to keep out the sound, while the three shafts turning the screws of the interferometer adjustment protruded through sound-tight fittings. Upon the front of the instrument a properly tuned resonator was attached, and at the side was a small incandescent lamp with a straight, horizontal filament, an image of which was projected by a lens upon the first mirror of the interferometer. Upon this was focused a telescope, giving in the reticule an image of the horizontal, straight filament, crossed by the vertical interference fringes seen with white light. In order to get these the plate must be in the proper position within a few hundred-thousandths of an inch. The objective of the tuning-fork was carried by a tuning-fork which oscillated vertically, tuned to the pitch of the pure tone to be examined, and this, combined with the horizontal motion of the fringes, resulted in a figure of coloured fringes in the form of an ellipse. On slightly mistuning the fork, the ellipse could be made to go through all its phases, and when it was reduced to an inclined straight line its inclination was read off on a tangent scale. The amplitude of the compression of the air in the sound was then directly proportional to the scale-reading.

While the interferometer is still used for calibration, the movement of the diaphragm is recorded for actual measurements by a thin steel torsion strip carrying a concave mirror. A lamp with a vertical, straight filament is viewed through a telescope into which the small mirror focuses the image of the filament on the reticule, and a magnification of from 1200 to 1500 is used, so that the sensitiveness is about the same as with the interferometer.

At first the only method of tuning was the clumsy one of changing the mass of the diaphragm by adding small pieces of wax. This was not capable of continuous variation. Now the diaphragm has been discarded and replaced by a rigid disc supported by three steel wires in tension. The disc is made of mica or aluminium, and is carried by a little steel spider containing three clamps to hold the wire. The tension is regulated by three steel pegs, one of which is controlled by a micrometer screw. The disc is placed in the circular hole through which the sound enters the resonator. This has the advantage of reducing damping very largely, and thus of increasing the sensitiveness enormously. The instrument now competes with the human ear, and can be tuned over two octaves or more.

This sensitiveness can be demonstrated by projecting the coloured interference fringes on a screen and singing faintly in a remote part of the room, when the fringes will disappear. Using the telescope end of the apparatus, the instrument will indicate the sound of a tuning-fork when one can scarcely hear it. It is obvious that the disc may be made the diaphragm of a telephone and thus increase its sensitiveness. In fact, Prof. King has used such a telephone to record wireless messages with great success. He has also invented another sort of tunable diaphragm composed of a stretched steel membrane with compressed air behind it, which enables it to be tuned continuously, but over a smaller range.

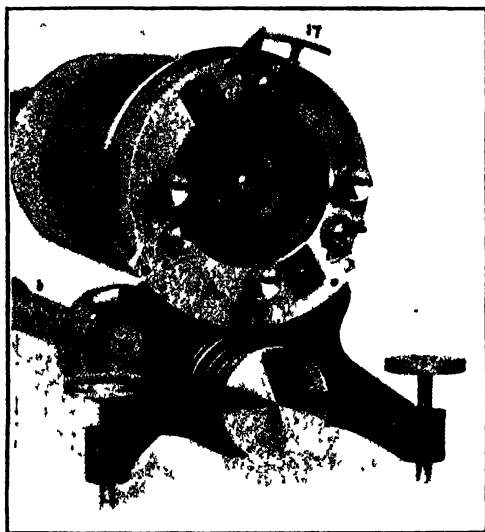


FIG. 3.—FRONT VIEW OF PHONOMETER WITH ANNULAR OPENING.

I now come to the source of sound—the phone. This has been reduced to a reversed form of the phonometer. The disc is driven by an interrupted or alternating current by means of electromagnets, and tuned like the phonometer. Its excursion is measured by a powerful microscope, and the emission of sound is known in absolute measure. It is now driven by a triode valve tube, in the manner suggested by Prof. W. H. Eccles, of Finsbury Technical College, London, for a tuning-fork. This has been worked out for me by Dr. Eckhardt at the Bureau of Standards in Washington.

The third part of the investigation involves a determination of the coefficient of reflection of the ground. The phone is set at a convenient height, and the phonometer at a convenient distance.

Either is then moved along at a constant height and the varying deflections of the phonometer are read while the sound remains the same. Interference sets in between the direct sound and its image reflected in the ground, and the existence of a minimum is obvious to the most naive observer by the ear alone. The reflection of either grass or gravel was found to be about 95 per cent., while, with a most carefully deadened room, the walls of which were covered with thick felt, there was perhaps 20 per cent. reflection. The whole measurement at both ends and the transmission checks up with an accuracy of about 2 per cent.

With this apparatus all sorts of acoustical experiments may be performed. By attaching to the phonometer a long glass tube or antenna, it has been possible to explore all sorts of places, such as the field within a horn or tube lined with an absorbent substance. The transmission of sound through fabrics, walls, and telephone booths may also be quickly examined. The instrument is used by psychologists and by telephone and acoustic engineers, and is of interest to navigators. An interesting by-product is an instrument for showing the direction of an acoustic signal in the fog. It has been called a phonotrope, on the analogy of heliotrope, which turns to the sun. It consists of two equal horns which bring the sound to the opposite sides of the disc. When the whistle blows, the band of light spreads out, and on turning the instrument it closes to zero when the sound is directly ahead. Thus at several miles the direction is given to within two or three degrees.

Finally, let us consider that mystery of sound, the violin, which has been studied by Prof. Barton, of Nottingham, and by Prof. Raman at Calcutta. This may be described by the engineer as a box of curious shape, made of a curious substance, wood, of variable thickness, with two holes of strange figure to let the sound out of the resonating box. The latter is actuated by a curious substance, catgut, made of the intestines of a sheep, and set in vibration by another curious substance, the tail of a horse. Yet from this wonderful box we get the most ravishing sounds, which affect profoundly the emotions of the most civilised. Yet the physicist reduces all musical instruments to combinations of resonators with strings, membranes, bars, plates and horns. The mathematical theory of strings was given by Euler two hundred years ago, of bars and plates less than a hundred years, of resonators by Helmholtz and Rayleigh, and I have recently added a theory of horns which, while only approximate, works well in practice, and investigations are now being carried out by such methods on vowels and the violin.

[A. G. W.]

Friday, March 10, 1922.

COLONEL E. H. GROVE-HILLS, C.M.G. D.Sc. F.R.S.,
Secretary and Vice-President, in the Chair.

THOMAS R. MERTON, M.A. D.Sc. F.R.S., Professor of Spectroscopy
in the University of Oxford.

Problems in the Variability of Spectra.

[ABSTRACT.]

It has been known for many years that the radiations which an element emits in the state of a luminous gas are not invariable, but depend on the presence of other elements, the manner in which the substance is excited to luminosity, and other circumstances. It was recognised in some of the earliest investigations that many band spectra were to be associated with compounds, and that a spectrum might be due partly to such compounds and partly to uncombined atoms. Thus, for example, if strontium chloride is introduced into the flame of the Bunsen burner we find lines associated with the element, bands due to strontium oxide, and also bands due to the chloride, and when strontium bromide is substituted for the chloride the spectrum is the same as regards the lines due to the element and the oxide bands, but bands peculiar to the bromide are found to have replaced those due to the chloride. Minute quantities of substances can sometimes be detected by means of these characteristic bands due to compounds, a familiar example being the blue flame which is seen when common salt is thrown on to a coal fire, and which is due to the copper chloride formed from the chlorine in the common salt and the minute trace of copper which is present in the coal. A number of different elements are present in most flames, and the reactions which occur are probably very complex. In gases contained in vacuum tubes which are excited to luminosity by electrical discharges, it is possible to work with pure substances, and a discussion of the spectra observed is simpler.

In the case of gases in vacuum tubes the spectrum sometimes consists of bands, and the band spectrum from the negative pole may be different from that seen in the positive column. Thus nitrogen, when excited by uncondensed discharges, shows in the visible

regions two band spectra—one known as the positive band spectrum, which appears in the capillary of a vacuum tube of the conventional type; and the negative band spectrum, which is found in the neighbourhood of the cathode, and which constitutes an important part of the spectrum of the aurora. Both these band spectra, and indeed all band spectra, are generally attributed to molecules rather than atoms; but if a condensed discharge is passed through nitrogen the spark spectrum associated with the nitrogen atom is obtained, and this is capable of further modification when discharges of great intensity are employed. The action of the condensed discharge is almost certainly due to the greatly increased current density which obtains during the very brief periods while the discharge is passing, and its first effect is to break up the molecules into atoms, and the further stages brought about by an increase in the intensity of the discharge are generally supposed to be due to the removal of successive electrons from the atoms. There are other methods by which the current density can be increased with similar changes in the spectrum, the effect of an increase in the current density being to increase the number of charged particles in a given volume of the gas, with the result that a large number of the radiating atoms are subjected to intense electric fields due to neighbouring charged particles.

Similar results are observed in the spectra associated with carbon. There are at least six spectra due to compounds of carbon with hydrogen, oxygen and nitrogen, and special experimental conditions are necessary for the production of some of these spectra. In addition to these band spectra carbon shows line spectra, and with the most intense discharges which can be employed in the laboratory a number of new lines appear which are also found in the spectra of the hottest type of stars, known as the Class O, or Wolf-Rayet stars. All these changes can be reasonably accounted for, but there are a number of other changes which are more difficult to explain. For many reasons the spectrum of hydrogen is of particular interest, because the atom of hydrogen is the simplest known atom, and is supposed to consist of a positive nucleus and a single electron. There are two spectra associated with hydrogen, one of which is known as the Balmer series and is found in almost all celestial spectra, and also in vacuum tubes in the laboratory unless the most rigorous precautions are taken to exclude all traces of hydrogen. The explanation of the origin of this spectrum has been one of the most striking successes of the quantum theory of spectra developed by Bohr and by Sommerfeld. The other spectrum of hydrogen, known as the secondary spectrum, consists of an enormous number of lines, and differs in its mode of production from the Balmer series in that the secondary spectrum is characteristic of pure hydrogen. In the purest hydrogen obtainable the secondary spectrum may be as bright as the Balmer series, but if the smallest trace of impurity is present the Balmer series gains in intensity and the secondary spec-

trum becomes very much weaker. In a vacuum tube containing water vapour the lines of the Balmer series are extremely intense, whilst those of the secondary spectrum are relatively very faint. The investigations of Michelson and Lord Rayleigh, and of Buisson and Fabry, have shown that under certain conditions the masses of the atoms or molecules from which the spectrum originates may be deduced from a knowledge of the widths of the spectrum lines, and recent investigations, in which the widths of the lines of the secondary spectrum of hydrogen have been measured to a high degree of precision, have shown that the secondary spectrum is to be referred to the hydrogen molecule. The presence of impurities in vacuum tubes containing hydrogen not only enhances the lines of the Balmer series, but also brings about changes in the relative intensities of the Balmer lines themselves. Some of these changes are very striking, but there are other variations of a more subtle kind, which are only discovered when accurate quantitative measurements are made of the relative intensities of the lines. A most striking effect is observed when a relatively large quantity of helium is admitted to a vacuum tube containing hydrogen. Under these conditions the relative intensities of some of the lines of the secondary spectrum alter in a surprising manner, some of the lines being greatly enhanced, whilst others become very weak.

From a theoretical point of view the spectrum of helium is second in importance to that of hydrogen only. The lines of helium are prominent in the spectrum of the chromosphere of the sun and of many stars, and their relative intensity varies under different conditions of excitation in the laboratory and in different celestial spectra. There are six chief series of lines in the spectrum of helium, three of which are usually referred to as the helium and three as the parhelium series. The helium series are the stronger in vacuum tubes containing the gas at pressures exceeding a few millimetres, whilst at very low pressures the parhelium series are predominant; and since the chief visible line of the helium series is yellow, and that of the parhelium series green, the colour of the discharge is changed from yellow to green when the pressure is reduced. There is another spectrum associated with helium which is analogous to the secondary spectrum of hydrogen in that it only appears with any considerable intensity when the gas is exceedingly pure. This spectrum is known as the band spectrum of helium, and its occurrence in a gas which is known to be incapable of forming molecules, in the chemical sense of the word, is very remarkable, in view of the fact that band spectra are generally attributed to molecules. It may perhaps be suspected that there is some temporary association of atoms during the passage of the electric discharge which cannot be referred to as a molecule in the chemical sense of the word. Professor Fowler has shown that the arrangement of the heads of the bands in this spectrum resembles that found in series of lines

which are due to atoms, though the arrangement of the lines which constitute each band is of the type usually found in band spectra. When powerful condensed discharges are passed through helium a spark spectrum is developed. Two series in this spark spectrum are known as the 4686 and the ζ Puppis series, and their discovery by Professor Fowler has led to some of the most important developments of theoretical spectroscopy. These spark lines of helium are found in the nebulae and early type stars, and are attributed to helium atoms which have lost an electron.

The energy required to produce spark spectra varies widely with the nature of the gas under investigation, and for elements of the same chemical group is, as a rule, smaller the greater the atomic weight of the element. Thus, in the case of helium powerful discharges are required for the production of the spark spectrum, and the lines of the arc series are always bright. In the case of argon a much less intense discharge is required to produce the spark lines, and with very powerful discharges the arc lines disappear almost entirely from the spectrum. In addition to the production of these spark spectra one of the effects of powerful condensed discharges is to alter the relative intensities of the arc lines. Generally speaking, the effect of an increase of energy on a particular series of lines is to enhance relatively the more refrangible members of the series, but the effect varies in degree for different series. Experiments of this kind enable us to imitate to some extent in the laboratory the distribution of intensity amongst the lines which is found in nebular and stellar spectra. It will be seen that whilst many variations in spectra can be referred to different compounds, to molecules, and to uncombined atoms in successive stages of ionisation, there are a number of other changes for which there is at present no obvious theoretical explanation. The possibility of some specific influence of one gas on the spectrum of another must now be recognised apart from the formation of chemical compounds, which, in the action of helium on the spectrum of hydrogen, appears to be excluded. There is other evidence, based on a study of the broadening of spectrum lines, of a specific action on neighbouring atoms. We are still awaiting a satisfactory theoretical explanation of phenomena of this kind, though it is now forty years since what is perhaps the first known example, the action of sodium on the absorption spectrum of magnesium vapour, was observed by Professor Liveing and Sir James Dewar in this Institution.

[T. R. M.]

Friday, April 28, 1922.

SIR JAMES REID, Bart., G.C.V.O. K.C.B. M.D. LL.D.,
Vice-President, in the Chair.

ARTHUR HARDEN, D.Sc. F.R.S.

Vitamin Problems.

[ABSTRACT.]

THE existence of three vitamins, termed A, B, and C, has now been firmly established, and a general idea has been obtained of their distribution among animal and vegetable organisms. Hitherto, comparatively little quantitative work has been done in this direction, and further progress must depend on a more general adoption of quantitative methods. These are at present tedious and not very accurate. In the case of each of the vitamins the requirements of the special animal employed serve as the unit of comparison, and these vary considerably from individual to individual, so that many observations are necessary if any, even moderate, degree of accuracy is to be attained. Thus in the estimation of the antiscorbutic potency of food materials, by the method worked out by Miss Chick and her colleagues at the Lister Institute, it has seldom been possible to achieve a greater accuracy than about 25-50 per cent. This obviously imposes a very serious limitation on any attempts to study variations in potency unless these are of a very gross order. Another great difficulty inherent in this kind of observation is that when the potency is low, the necessary dose of the material to be tested is correspondingly high, and soon transcends what is permissible without interference with other necessary conditions of the diet, such as protein content, etc. Very much the same conditions hold with regard to Vitamin B, especially when this is estimated by the effect of the material on the growth of rats; and, as a matter of fact, the great bulk of the work carried out in America by this method is not strictly quantitative, but simply leads to the result that a certain ration does, or does not, suffice for the growth of a young rat.

As regards Vitamin A, the method of Zilva and Miura promises to yield moderately accurate and consistent results. This is attained by keeping the experimental animals (young rats) on a diet totally deficient in Vitamin A until they have ceased to grow, and then

ascertaining the minimum dose of the material to be tested which will induce definite and steady growth for four weeks. Animals which do not cease to grow in three weeks are rejected, greater uniformity in the results being thus attained. The test material is, whenever possible, administered quantitatively to the animal, and not, as was formerly the practice, mixed with the ration in a known proportion. One of the immediate results of the application of this method has been the discovery that cod-liver oil, formerly classed with butter as a good source of Vitamin A, is in reality 200-250 times as potent as butter, and is, along with similar fish-liver oils, by far the richest in this material of all the substances which have so far been examined.

A further piece of information, which is essential for the detailed study of these substances, is their behaviour towards heat, oxidation, etc. In this respect some progress has been made, and it may be stated with some confidence that both Vitamins A and C are moderately stable towards rise of temperature, provided that air be excluded, whereas in the presence of air they are rapidly inactivated. Whether the effect of air is reversible or not has not yet been ascertained. Vitamin B, on the other hand, appears not to be affected by air, and is also moderately stable towards rise of temperature. None of the three vitamins is easily inactivated by hydrolysis under anaerobic conditions, and this fact has led to the interesting observation that Vitamin A, although usually associated, in the animal organism, with fat, is not itself a fat, but remains in the unsaponifiable residue with almost unabated potency. This indicates how small a weight of the vitamin itself is necessary for the daily ration of a young rat. In some cases as little as 1.2 milligram of the oil is sufficient to permit of definite growth, and of this only 1-2 per cent. is unsaponifiable, while, as is well known, the chief constituent of the unsaponifiable matter is cholesterol, which has itself no vitaminic potency. The actual requirement of the vitamin itself must therefore be of the order of $1/500$ milligram per diem. The other two vitamins have not been obtained in so concentrated a form, but it appears highly probable that they too are present in foodstuffs only in infinitesimal amounts.

The origin of all three vitamins is to be sought in the vegetable kingdom. The production of Vitamin A has been followed (Coward and Drummond) from the seed, and it has been found that it does not appear until the photosynthetic processes begin. Thus sunflower seeds are almost devoid of it, and so are the etiolated seedlings formed when these seeds germinate in the dark. In the light, on the other hand, the green seedlings, grown in a medium free from the vitamin, produce it freely. This vitamin is often closely associated with the carotene and xanthophyll of plants; so intimately indeed, that it was at one time thought that it might be closely related to, if not identical with, one of them. The association, however, although very frequent,

is not essential, and no definite relation can be shown to exist between the two. Vitamin C is either absent from seeds or only present in them in very minute amount, but appears when the seed germinates and before any green parts are formed. Nothing is, however, known of the inactive pro-vitamin or of the process by which it is rendered active.

Concerning the origin of Vitamin B a considerable amount of discussion has taken place. Its presence in a large proportion in yeast points to the probability that it can be produced without the intervention of light, and both in America and in this country it has been found that yeast can actually produce the vitamin when grown in a "synthetic medium" comprising only substances of known composition and free from the vitamin in question. Recently, however, Eijkman, in Holland, has obtained a contrary result, so that at the moment this remains an open question.

The animal organism appears to be unable, in normal circumstances, to produce any of these principles for itself, and hence the amounts found in animal products depend ultimately on the diet of the animal. This opens up, among many other problems, the important question of the vitaminic properties of milk, and there seems to be no doubt, from experimental work, both here and in America, that these properties are profoundly affected by the diet of the cow. Milk obtained in winter when the animals are stall-fed has been shown to be markedly deficient in Vitamin A, and there is also great danger of a deficiency of Vitamin C. One of the pressing requirements of the moment is the careful quantitative examination of foodstuffs available for the feeding of cattle, so that a rational system of winter feeding can be adopted which will produce milk as good as that given in summer. Such an examination would seem naturally to fall within the purview of the Board of Agriculture.

The evil results of a deficiency of Vitamins B and C, especially in the diet of children, are well known--beri-beri and scurvy, latent or patent--but the effect of a lack of Vitamin A is not so well recognised or so universally acknowledged. One school considers that a deficiency of this vitamin is at least a prominent factor in the causation, if not, as they formerly held, the sole cause of rickets. Others consider rickets to be a disease brought on by non-hygienic surroundings, lack of fresh air and exercise, etc. The latest experimental results show that rickets (in rats) can be produced infallibly by dietetic changes, but that the lack of Vitamin A does not of itself lead to the disease unless at the same time the diet is faulty as regards the supply of calcium or phosphorus. This faulty mineral supply does not usually lead to true rickets if sufficient Vitamin A be present, although the bone formation under these circumstances is not quite normal. This explains the well-known curative effect of cod-liver oil in rickets. So marked is the effect of this remedy, that McCollum, not appreciating the relatively enormous concentration of Vitamin A

present in it compared with that in butter, as proved by Zilva, has suggested that cod-liver oil contains some other specific substance absent from butter, to which its great superiority is due. The difference, however, seems to be merely quantitative, and the further complication suggested by McCollum appears to be unnecessary.

These experiments on rickets have led to what promises to be a discovery of far-reaching importance. Rats on a diet, which in the laboratory will infallibly produce rickets, do not acquire the disease if they are exposed to sunlight in the open air or to ultra-violet radiation, and rats which have acquired the disease can be cured by either of these treatments, just as they can be cured by the administration of cod-liver oil. Sunlight and ultra-violet radiation have also been found to be effective cures or preventives of rickets in children. The cures by light and by cod-liver oil seem to proceed in precisely the same way, and the idea naturally suggests itself, especially to the mind of a chemist, that the light actually brings about the synthesis of the vitamin in the animal body just as it does in the plant. This idea still awaits experimental verification or disproof; but there is no doubt that this function of light will lead to profoundly important developments in our knowledge.

[A. H.]

Friday, May 19, 1922.

SIR J. J. THOMSON, O.M. M.A. LL.D. D.Sc. F.R.S.,
Honorary Professor of Natural Philosophy R.I.,
Vice-President, in the Chair.

SIR WILLIAM BRAGG, K.B.E. D.Sc. F.R.S. M.R.I.

The Structure of Organic Crystals.

It may be said with truth that modern advances in physical science are due in the main to the acquisition of the power to handle the individual atom. Until the present time we have always attacked the problems of matter by examining the behaviour of atoms or molecules in groups. The new powers arise in two ways :—

In the first the individual atom is endowed with excessive speed and energy, and is able to make its individuality felt on this account. The α -particle of the radioactive radiations is a helium atom moving with a speed of the order of one-tenth of that of light. While in possession of the relatively tremendous energy which the speed implies it can, unaided, make a visible impression on a fluorescent screen. It can pass through thousands of other atoms without sensible deviation, and if occasionally it suffers violent deflection it has penetrated to the very core of the atom which has deflected it. Rutherford has shown us what important deductions can be drawn as to the construction of the atom by examining these rare and sharp deviations, and is going even further in examining the shattering effect which the deflecting atom may itself experience. So also, the electron endowed with sufficient speed can transverse matter and bring about ionisation and other effects of great interest, but if its velocity becomes less than one million metres per second this free existence disappears. It is attached to the first atom it meets.

The second method of attack upon the individual atom proceeds on very different lines. It is by way of the mutual action of X-rays and crystals. When we are examining things by eyesight we follow the influence of the objects that we look at upon the waves of light. If we wish to penetrate deeper into the minute, we take advantage of the optical effects of lenses and build microscopes : but, even then we cannot attack individual objects containing less than many thousands of individual atoms. A limit is set by the difficulty that light cannot show us the form of things which are much smaller than the wave length of the light itself. With the aid of the very short

waves known as X-rays we can make our way down to objects ten thousand times smaller, but by itself this extension of our powers would be inefficient, because the effect due to one atom or one unit of pattern would be inappreciable. Here lies the value of the crystal, which, being an aggregate of some small atomic pattern repeated again and again through space, shows up on a measurable scale the properties of the atoms in the single unit. By the combination of X-ray and crystal we can examine the very foundations of material construction. It is difficult to set a limit to what may be the consequences of the exercise of these powers since we can now examine all physical effects, so to speak, at their source, and must in the end be able to refer all the physical and chemical properties of materials to the properties of the individual atoms and their mutual forces. So far the new methods have scarcely begun to show their full strength. A few inorganic crystals have been examined with a view of discovering their structure, but the new field of research is barely entered. Inviting roads lie before us pointing in numerous directions.

Very little has yet been done in the way of applying the new methods to the structure of organic crystals, although no study could be more tempting. Their vast variety of form, the perfection of their structure, their importance, all urge us forward, and especially the fact that the whole progress of organic chemistry shows that the science depends upon laws of position with which the X-rays are especially qualified to deal. The difficulty at the outset lies in the complexity. In the naphthalene molecule there are eighteen atoms: in what way can we expect by means of X-rays to solve the intricate problem of their relative positions? Our first attempts to solve inorganic crystals depended for their success upon two facts:—

The first, the simplicity of the structures which were attacked.

The second, the guidance derived from the principles of crystallographic symmetry.

The determination of the structure of rocksalt opened a way to further determinations of such simple crystals as the diamond, zinc blende, fluorspar, and others. In all these the principles of symmetry supplemented the knowledge derived from the examination of the intensities of X-ray reflection by the various crystal planes. As the work has proceeded in the hands of observers in many countries, other principles have emerged or are emerging which render further and very valuable aid, so that problems appear to be coming within our grasp that not long ago seemed most difficult of solution.

Of these principles, one began to appear in consequence of the very earliest results. It was a very striking fact that in crystals of polar substances the molecule seemed to disappear; it was in fact dissociated, and the structure of the crystal depended upon the grouping of the positive ions round the negative and of the negative ions round the positive. In rocksalt each metal atom is surrounded by six atoms of chlorine and vice versa. If we accept this as an

indication of the general character of such structures, adding to it the condition that every atom is to be like every other atom of its own kind in respect to relative distances and orientations of all its neighbours, it becomes possible to foretell the probable form of structure, using the X-ray methods for subsequent verification. This method of proceeding may be very much easier than if it were taken in the reverse way. We might, for example, have gone far to foretell the structure of fluorspar. It is an ionic compound in which the calcium atoms are doubly charged and fluorines are singly charged. Each positive is to be surrounded, therefore, by twice as many neighbours as each negative by positive. The fluorspar structure in which the metal atoms are arranged at the corners and the face centres of the cube, while the fluorines lie at the centres of the eight small cubes into which the larger ones can be divided, is one of the very few regular ways in which this numerical relation of 2 to 1 can be carried out. So also in ice, the 2 to 1 arrangement is carried out in a second of these ways, the relative numbers being 4 to 2. It is the lightest and most open of the 2 to 1 structures, and is consistent with the low specific gravity of ice and with the possibility of compressing the substance into denser forms : at the same time it shows the six-pointed arrangement and the featheriness of the snow crystal.*

The earlier results at the same time showed that in the diamond we had a construction of very different properties and nature. Here the atoms are electrically neutral and are bound to one another, not by electrical attraction from centre to centre, but by a more intimate process which probably consists in some way of a sharing of structural electrons. The diamond is on this account the hardest of known substances.

These considerations amount to a recognition that the bonds between the atoms may be of very different characters, though it may be difficult to draw hard-and-fast lines between them. We can say that there is a very strong electron-sharing bond of which the diamond is typical, and that there are ionic bonds in polar compounds which in general are of a weaker character, as, for example, in rock salt, though on the other hand they may be strong when, as in the ruby, the ionic charges are large.

Lastly, there is a third type, which is found in the organic crystal, where it would appear that the separate molecule can be distinguished. The atoms in each molecule are strongly tied together, but the forces that bind molecule to molecule may be described as residual. They would appear to be weak fields concentrated at definite points on the molecule, the positive and negative charges to which they are due lying within it.

The second principle, which emerged fairly early in the experiments, was described by my son in an address which he gave in this

* Proc. Phys. Soc., London, vol. xxxiv. pt. 3, p. 98.

Institution some time ago.* We may call it the principle of radii of combination. The distance between the centre of one atom and the centre of a neighbour in many cases can be measured with great accuracy; we can compare these distances when substitutions are made in isomorphous compounds. The replacement of fluorine by chlorine, chlorine by bromine, bromine by iodine in a series of salts produces changes in the distances which imply that the radius of any one of the atoms mentioned may be treated as a constant within the range of the substitution considered. The accuracy is amply sufficient to give useful assistance in crystal analysis. It would not be true, however, to say that each atom has an invariable radius, and indeed the original statement of the principle purposely refrained from going so far. It is not right to speak of *the radius* of an atom; it is better to speak of *a radius of combination*. We may take an illustration from the behaviour of arsenic, antimony, and bismuth. The crystals of these substances are trigonal in form,† plainly showing that the properties of each atom are not the same in all directions within the crystal; in fact, analysis shows that each atom is fastened to three on one side of it by much closer bonds than to three atoms on the other side. One bonding resembles more closely that of the diamond, the other that of a metal where free electrons keep the atoms together by electrostatic attraction. It may be said that the atom behaves as a metal on one side and a non-metal on the other. At any rate, there are two radii of combination varying with the nature of the bond. The metallic bond is the weak one, and the cleavage plane cuts only through such bonds. It seems very likely that in this way we can understand the formation of crystals of different type when these elements enter into their composition. For example, in the cubic form of senarmontite (Sb_2O_3) the atoms of antimony are completely separated; each touches six atoms of oxygen, while each oxygen touches four atoms of antimony. Antimony is here behaving as a metal only, so that we represent it in a model as a sphere, and the uniform spheres of antimony and of oxygen naturally build into a simple crystal. It is a cube in which the atoms of antimony occupy the corners and centres of the faces, while the six oxygen atoms lie at the centres of six of the eight small cubes into which the large one can be divided.

There is, however, an alternative form of Sb_2O_3 known as valentinite, which is ortho-rhombic. Analysis, so far as it has gone, though it is not yet complete, points emphatically to the conclusion that here atoms of antimony are pairing, the bonds between the members of a pair being of the stronger variety already referred to.

* See Phil. Mag., Aug. 1920.

† James and Tunstall, Phil. Mag., Aug. 1920 and July 1921; Ogg, Phil. Mag., July 1921.

We now have an elementary body of a dumb-bell shape which, when forming part of the crystal structure, will naturally cause a deviation from a simple cube.

Again, there are principles which are barely established as yet, though it seems probable that they will be found of material assistance in analysis. The greater expansion of some crystals in certain directions than in others seems to depend upon the nature of the bonds. Bismuth expands more along the axis than across it, as we might expect from the fact that in the one expansion the weak bonds alone can be operative. In the same way diamond has an extremely small expansion co-efficient because all the bonds are of the strongest kind, but in graphite, on the other hand, the expansion along the axis may be described as enormous. Mr. Backhurst finds an increase in length of 3 per cent. for a rise of 900°C . At the

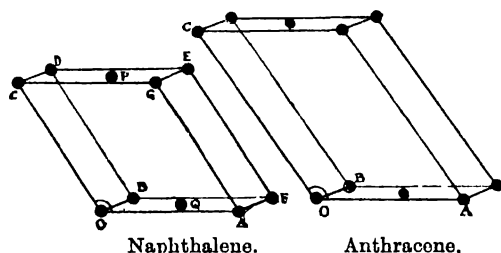


FIG. 1.—Unit cells of naphthalene and anthracene drawn to the same scale.

	OA = a.	OB = b.	OC = c.
Naphthalene	8.84	6.05	8.69
Anthracene	8.7	6.1	11.6
Naphthalene $\alpha = \text{BOC} = 90^{\circ}$, $\beta = \text{COA} = 122^{\circ} 49'$, $\gamma = \text{AOB} = 90^{\circ}$			
Anthracene $\alpha = \text{BOC} = 90^{\circ}$, $\beta = \text{COA} = 124^{\circ} 24'$, $\gamma = \text{AOB} = 90^{\circ}$			

same time, so far as can be inferred, the expansion across the axis is still quite small. In one case weak bonds only are concerned, in the other strong bonds of the same kind as in the diamond.

It is when all these considerations are taken into account that it seems possible to make an attempt upon the structure of the organic crystals. They are, of course, very complex; naphthalene contains ten atoms of carbon and eight atoms of hydrogen, and our ability to interpret X-ray evidence, that is to say, the relative intensities of reflection by the different planes in different orders, is not sufficiently advanced to place so many atoms in their proper position in the cell from this evidence alone. We can readily find the size of the unit cell, show that there are two molecules in it, and that the points, each of which represents a whole molecule, are to be placed as is shown in Fig. 1, but without some further help we can frame no hypothesis on which to proceed.

Suppose now that we compare the structures of diamond and graphite. As my son showed long ago, the structure of graphite must be derivable from that of the diamond by separating to nearly double their previous distance the sheets of atoms parallel to one of the cleavage planes of the latter crystal. The question has been very carefully considered more recently by Hull in America and by Debye and Scherrer on the Continent in the hope of finding more exactly the details of the movement; they do not quite agree. Fig. 2 represents the change as described by Hull. The bonds between the atoms in each sheet are unaffected apparently, but those between sheet and sheet are replaced by something much weaker. The diamond is typical of hardness; the graphite is used as a lubricant. If the hexagonal rings of which the sheets are formed have survived this violent change, why not suppose that they may survive the further change when the sheets break up into ring structures?

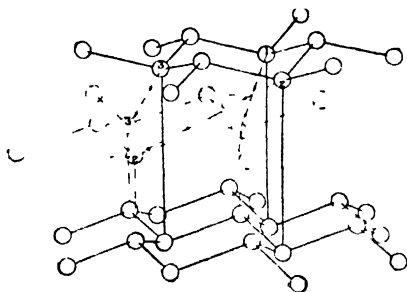


FIG. 2.—The fine lines of the diagram show the structure of graphite. By moving the top layer to the position shown by the broken lines the diamond structure is obtained.

In other words, suppose that the benzene ring is really a fact, not merely a diagram: the distance between atom and atom in the ring is 1.54 \AA.U. , as in the diamond, and perhaps we may add that the atoms are not all in one plane, but are arranged as may be seen in Fig. 3. We then proceed to test this hypothesis by finding whether we can fit together molecules of the assumed size and shape into the cells which hold them. From X-ray studies we know the exact form and dimensions of the cells, and can learn also much concerning the relative distributions of the molecules within them. It appears at once that in the few simple cases which have been examined an excellent fit is possible, and, more than that, we find encouraging signs that the structural idea has been chosen rightly. For instance, the comparison of the cells of naphthalene and anthracene, one a two-ring, the other a three-ring combination, shows that two of the axes of the cell remain constant, while the third has grown by an amount

which is nearly the width of the benzene ring. From these and various other indications we build a structure such as is represented in Figs. 3 and 4. It would seem that the molecules are linked

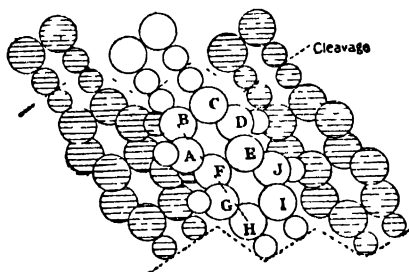


FIG. 3.—Showing mutual relations of three naphthalene molecules and parts of others.

The unshaded circles between the two cleavage planes represent a molecule as at Q (Fig. 1). The shaded represent molecules B and F in the same figure. The small circles represent hydrogen atoms, but their size is uncertain.

Diameter of carbon atom = 1.50. BH = 4.92. Projection of AD on the plane of the diagram = 2.50. Benzene ring consists of atoms A-F only.

together side by side more strongly than from end to end, and that is why these and similar crystals cleave across the end or β position.

If we examine α -naphthol in which hydrogen at the side of the naphthalene molecule has been replaced by an OH group, we find

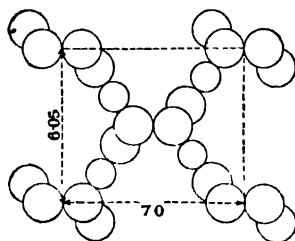


FIG. 4.—Section of naphthalene cell perpendicular to the axis of c , showing α -hydrogens connecting the molecules side to side.

that the standard cell contains four molecules, which is what we should expect, for each of the four α positions must be represented. When the OH group is taken from the side and put at the end, we find that the cell has shrunk sideways and grown lengthways by the amount we should expect to result from the addition of an oxygen

atom. When as in acenaphthene a complex group of atoms is attached to one side of the molecule, and the crystal to our surprise becomes more regular than before, right-angled instead of oblique, we find an explanation in the fact that there are now four molecules within the cell instead of two, and that by sloping in pairs in opposite ways they increase the symmetry of the crystal.

These examples may serve to show how an attempt may be made to arrive at a knowledge of the structure of these organic compounds with, I think, some success. It seems justifiable to see in the rigid and qucerly shaped molecule attaching itself at definite points, and with great precision of orientation to neighbouring molecules, a cause of the immense multiplicity and, at the same time, the accurate form of organic crystals, and indeed to find here the foundations of organic chemistry.

[W. B.]

Friday, January 19, 1917.

HIS GRACE THE DUKE OF NORTHUMBERLAND, K.G. D.C.I. F.R.S.,
President, in the Chair.

PROFESSOR SIR JAMES DEWAR, LL.D. D.Sc. F.R.S.,
Fullerian Professor of Chemistry.

Soap Bubbles of Long Duration.

AN investigation of the properties of Soap Bubbles is the logical outcome of the experiments on flat liquid films described in the 1916 Friday Evening Discourse. Some fifty years ago Joseph Plateau—Professor of Physics at Ghent—began a series of investigations on Surface Tension Phenomena, and for nearly forty years carried out a number of wonderful investigations, although practically blind, owing to an accident which occurred while examining the action of intense light on the retina in the early part of his career. It is due to the fascinating character of his pioneer work on soap bubbles that the study has been continued. Since the work of Plateau great advances have been made in the experimental study of Surface Tension Phenomena by Dupré, Mensbrugghe, Reinold and Rucker, Michelson and his collaborators. The theoretical advancement which science owes to Willard Gibbs dominates all modern research on capillary phenomena.

The flat films described last year were developed in an exhausted atmosphere of nearly pure water vapour; while soap bubbles are blown up with air in air. Experiments extending over a year have proved that in order to keep soap bubbles for any length of time the air must be free from deteriorating gases and suspended solid matters. The presence of living organisms and their spores amongst the finely divided organic and inorganic particles in the atmosphere was discovered by Pasteur. He purified the air by passing it through a red-hot platinum tube containing platinum gauze, afterwards removing the total carbonic acid. Later Tyndall used a concentrated beam of light to demonstrate the presence of floating impurities in the air, as a test of "optical emptiness." Tyndall passed a parallel beam from an arc lamp through a large plano-convex lens, which condenses the light into a cone, at the apex of which the intensity of the illumination causes the floating matter in the air to be easily recognised. If a Bunsen or hydrogen flame is placed below the focus, the reflected light gradually disappears as the floating material, being largely organic, is burnt and passes into the atmosphere. Tyndall obtained a dust-free atmosphere by passing air through a red-hot platinum tube containing platinum gauze, afterwards removing the total carbonic acid. Later Tyndall used a concentrated beam of light to demonstrate the presence of floating impurities in the air, as a test of "optical emptiness." Tyndall passed a parallel beam from an arc lamp through a large plano-convex lens, which condenses the light into a cone, at the apex of which the intensity of the illumination causes the floating matter in the air to be easily recognised. If a Bunsen or hydrogen flame is placed below the focus, the reflected light gradually disappears as the floating material, being largely organic, is burnt and passes into the atmosphere.

Leyden jar spark (in place of the arc beam) the analysis of streaming patterns (formed by impinging air jets) into separate droplets was registered. Brilliant coloured photographs (Lumière autochrome) were secured by an exposure of $1/25$ second, which gave sharp definitions to the boundaries of differently coloured streams and zones.

Most of the early jets tried gave steady patterns on the films: these consisted roughly of a fine central straight stream line bending round at the film boundary into definite whirling vortices. Then some jets were observed to give recurrent spasmodic fluctuations as if occasionally obstructed. This was soon traced to disturbance by certain sounds acting on the air jets in a way similar to that shown by Tyndall's "singing flames." Finally, it was found that almost every jet could be made sensitive within certain limits of pressure of the air supply to it, jets with larger orifices being sensitive at low pressure and smaller ones at higher pressure. These fluctuations were also recorded photographically. The jet oscillations resulting from the sound pulses produced definite distortions of the fine steady stream line which the film showed with the jet undisturbed. Records were obtained in many cases showing varying distortions with different sounds. The beginnings of a method for analysing the wave forms of various sounds were thus established.

Before the study of these stream patterns, the magnified projection revealed many minute features of film development on a scale approximating to that of the Brownian motion: *e.g.* the formation of the black zone was seen to arise from the growth of minute black circular areas in all parts of the film, which coalesce as they pass through the thicker coloured portions and unite to form the black zone at the top. The rate of coalescence varies with different compositions of soap solution; successive spots follow single tracks through the film, and when sufficiently rapid form a continuous track like a black canal. A further stage has more than one canal, varying in width as larger or smaller black coagulations force their way up. The "banks" of the canals may then be ruptured and cross streams established at several points, changing in position and intensity, sometimes forming a quiet delta, or increasing to a network, either steady, or fluctuating through all stages of intensity up to a tumultuous development of rapidly oscillating torrents, or even to a complete disintegration into rapidly aggregating "islands" of thick coloured material in a very disturbed "sea" of black. The time of the complete process varies from several hours to a few seconds. The final rapid stage is a veritable explosion, ensuing usually after a more or less protracted initial quiet progress. It is then as if a black blind were drawn almost suddenly down over the coloured film, squeezing the colour down into a small colourless area below, or even into a single drop at the bottom, and leaving the film completely and intensely black.

Slow convection motions in quietly developed black films present many interesting features. An apparently black film is seen to have in reality a layer of extremely minute silvery misty particles, which can be made to coalesce to a greater or less extent into larger visible silvery stars, the drift of which over the deeper black film can be readily followed. These, with complete uniformity of conditions in the film vessel, slowly settle to a small but coherent silvery zone, steadily absorbed into the "Gibbs channel" (contact of film and support ring). By an air jet of carefully regulated intensity, a dainty silvery fountain can then be produced, drawn from the Gibbs channel and circulating like a nebula over the black film background. With a thick Gibbs channel and greater intensity of jet, the silvery stream is thickened through successive colour stages into gorgeous colour vortices, like butterfly wings or peacock feathers, sharply defined on the black film, while when the air jet is further intensified, a complete colour-banded film is built up as when first lifted from the soap solution.

By using larger but horizontal films, and special steatite nozzles pierced in several ways to give multiple jets at various inclinations, many stream-line patterns are obtained, through all stages of colour to black, reversible again to any colour stage. The very sharp definition of the stream lines, and the dainty outlining of the vortices, are the most remarkable features. With these films the simultaneous sensitivity of multiple jets can easily be shown.

SOAP SOLUTIONS.

For the studies of soap films to be described, many soap solutions were tried. Those made with ammonium oleate in diluted glycerin were usually found to be mobile and responsive to air jets at very small pressures; a slight excess of ammonia usually favoured this mobility, which was still pronounced even with concentrations of $6\frac{1}{2}$ per cent. ammonium oleate in 65 per cent. glycerin. In all cases a small excess of oleic acid was found to produce a viscous slowly developing film, even with very dilute solutions. This was an advantage when stable stream patterns were required. Solutions as dilute as 0.1 per cent. soap in 1 per cent. glycerin were quite workable.

Oleates of not only ammonium, sodium and potassium, but triethylamine and tetra-ethyl- and tetra-methyl-ammonium were very successful. They were all most carefully prepared, the last two from the bromides and silver oxide, filtered and added to an emulsion of oleic acid in the dilute glycerin. The chief difficulty lay in the preparation of reasonably pure oleic acid of anything like a standard quality. Apart from the elimination of other acids and unsaponifiable material elusive impurities remained which, despite an almost theoretical iodine number, sometimes gave a viscous or

slightly ropy consistency to the solutions, especially the ammonium preparations. By long standing a minute portion of the stringy scum could with care be separated from a 5 per cent. ammonium oleate solution in 50 per cent. glycerin (the standard preparation), but on dilution with "conductivity" water (*e.g.* to 2½ per cent. soap in 25 per cent. glycerin, and so on, down to 0.25 per cent. in 2½ per cent. glycerin, or even lower for some purposes) further turbidity and slight viscosity ensued. It was necessary to allow solutions to stand for several hours after dilution before they were reliable or uniform in behaviour. The tri-ethylamine soap

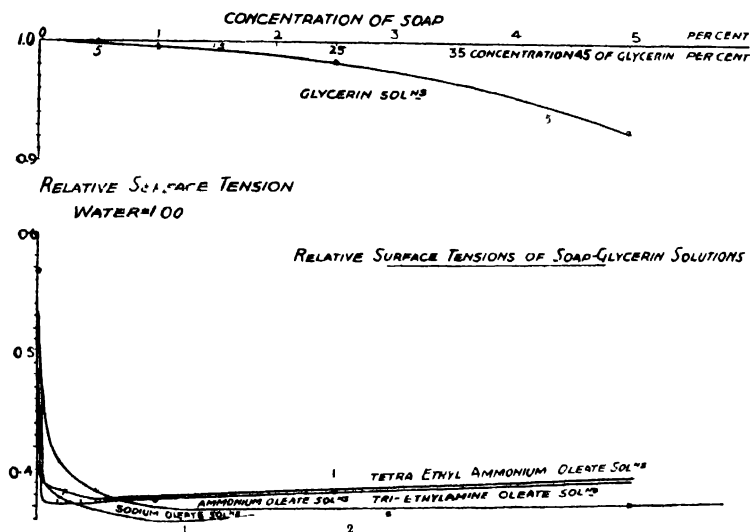


FIG. 1.

solutions were by far the most resistant to atmospheric impurities, and remained workable after considerable exposure in open bottles. Small admixtures of this solution greatly increased the stability of other solutions. The potassium oleates were very susceptible to traces of carbonic acid (as in the atmosphere). The ammonium soaps slowly became turbid and viscous through loss of ammonia, but as this could readily be corrected they were on the whole as useful as any. They are easily prepared without heating, which is very desirable when good clear colourless solutions are required. The manner and rate of thinning of the films varied greatly with different solutions.

The addition of a small quantity of soap reduces the surface tension of pure water to about one-third. It rises slightly, however, with increasing concentration of soap-glycerin. Fig. 1 shows the results for concentrations up to 5 per cent. soap in 50 per cent. glycerin, the soaps used being sodium, ammonium, tri-ethylamine and tetra-ethyl-ammonium oleates, the curves being numbered 1, 2, 3 and 4 respectively. The effect of the glycerin alone is shown by the top curve (No. 5). Large excess of oleic acid or ammonia has no effect on the surface tension of soap solutions, although 33 per cent. aqueous ammonia has a surface tension 75 per cent. of that of pure water

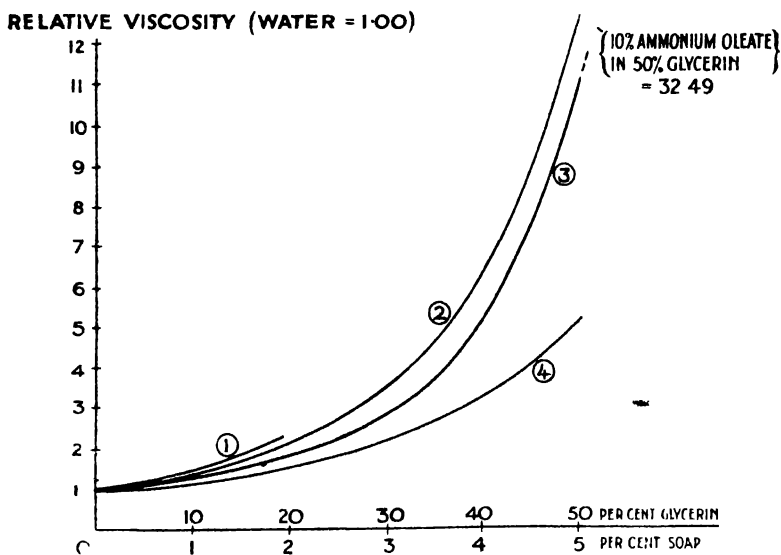


FIG. 2

The increase of viscosity with concentration of neutral soap-glycerin solutions is slow at first, and then very rapid above 4 per cent. soap in 40 per cent. glycerin. The glycerin is responsible for only about one-fourth of the total. Fig. 2 shows these results for solutions of (1) sodium oleate, (2) tri-ethylamine oleate, (3) ammonium oleate, (4) glycerin.

Fig. 3 shows the variation of viscosity with acidity or alkalinity of a 5 per cent. ammonium oleate in 50 per cent. glycerin. The increase due to excess acid is seen to be much greater than the decrease due to excess ammonia: the percentages are calculated on the amount present in neutral solution.

PRODUCTION AND DEVELOPMENT OF FILMS.

The films were produced on 8 cm. rings hanging vertically in an air-tight glass-sided box (Fig. 4), each edge of which was 1 ft. long. Petri dishes in the bottom of the cube contained the soap solutions, and the film was obtained by lowering the ring flat into the appropriate dish; a short bifilar thin chain suspension was found the simplest method for this purpose. The chain suspension was carried

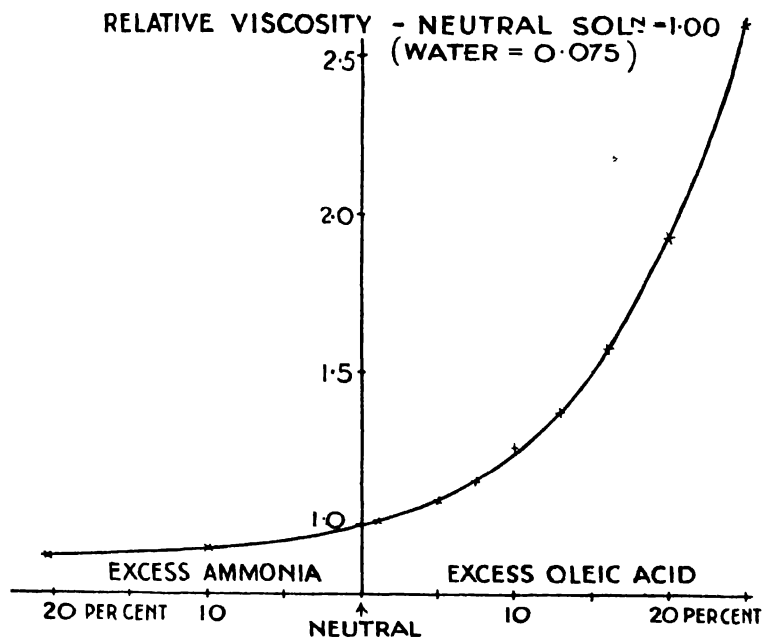


FIG. 3.

by a platinum fork sealed into a vertical glass rod sliding easily through a gland in the top of the cube. Suitable rings were made of platinum wire 1 mm. thick, or platinum-iridium wire 0.2 mm. thick, containing 10 per cent. iridium to make the thinner wire sufficiently rigid. The rings must be perfectly plane to give good reflections. The chain supports were fixed to two small loops welded on the ring about 3 cm. apart.

A uniform parallel beam of light, slightly wider than the ring, passed normally through one vertical glass side, and the reflection

from the film was made to pass normally through an adjacent side by setting the plane of the ring along the diagonal joining these glass sides. A lens of suitable focus then produced the image of the film surface on a screen or in the camera as desired. It was necessary to use a large glass water cell in the incident beam to prevent convection disturbances in the film. All light other than that of the restricted beam incident on and reflected from the film was absorbed by black screens fixed round the cubical glass chamber.

Air-tight glands in the top of the cube carried the ring support

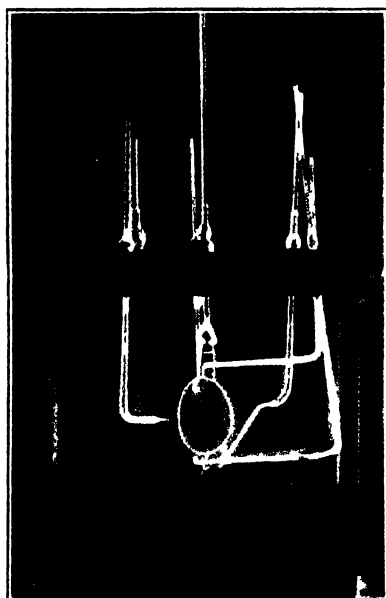


FIG. 4

rod, air jet, and drainage tubes and other fittings. These glands were simply made from bulbed glass tubes through which rods or jet tubes slid with a good but easy fit. They were blown out into a bulb finished above with a wider tube, having the space round the rod in the bulb uniformly packed with cotton wool moistened with glycerin. The wool packing was readily arranged to press sufficiently tightly to support the weight of the rod passing through without undue resistance to the necessary vertical adjustments, and the whole was supported by rubber corks through the top of the cube. The films were drained as required by a short bundle of folded platinum



FIG 5



FIG 6

wires (about 0.1 to 0.2 mm.) bound by a spiral of thicker platinum wire (0.4 to 0.5 mm.) sealed into the lower end of a glass rod sliding through one of the glands in the top of the cube.

When the film was first raised, and so thick that only very feeble colouring was seen in the ordinary way, a multitude of horizontal bands were readily shown by placing a cell of potassium bichromate solution in the incident beam. These bands were at first very

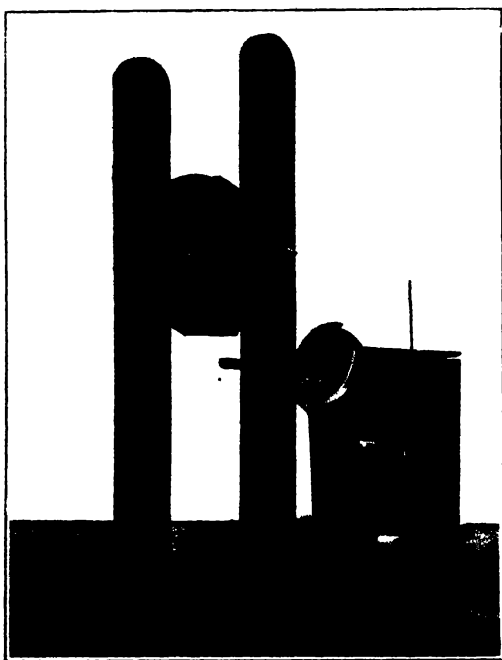


FIG.

crowded towards the bottom, and well spaced in the centre. The number of course decreased as the film thinned out. An early and a late stage are shown in Figs. 5 and 6. These occurred in less than four minutes with a diluted "Plateau" solution containing 14 per cent. sodium oleate in 12 per cent. glycerin.

These bands, when thus viewed in monochromatic light, are very suggestive of the absorption bands seen in the spectrum of white light reflected from a soap film, which were shown at the Royal

Institution by Thomas Young in 1802. A striking method of carrying out the demonstration is as follows :—The soap film is readily obtained by dipping a vertical wire frame into a cell of solution enclosed in a blackened wooden box, with a sliding plate glass front inclined out at the top to be about 10° from the vertical in order to deflect stray light from the path of the film reflected (Fig. 7). The wire frame is fixed to a light vertical rod passing through a clamp screw for raising and lowering and fixing as required. The film is placed in a parallel beam from an arc lamp directed slightly upward. The reflected light is focussed (6-in. focus lens) on a direct vision carbon bisulphide prism, supported in a stand with flexible adjustments for height and inclination. The refracting edge of the prism is horizontal, and therefore parallel to the lines of equal thickness in the soap film, which thus acts as its own slit. The brilliant spectrum thus obtained is crossed by sharp dark bands, very close together at first, when the film is thick and feebly coloured, but rapidly falling and spreading out as the film becomes thinner and more brightly coloured. These dark lines are caused by extinction in definite regions of the spectrum, corresponding to interference by reflections from the two film surfaces at certain thicknesses. When the film is freshly raised there is a great variation of thickness from top to bottom, and therefore many regions of interfering reflections, with resulting dark lines ; but few when the film thickness is more nearly uniform.

Reverting to the arrangement of Fig. 4, the development of a film can be watched at ease by projection in the laboratory upon a white screen some four or five yards away. A 12-in. focus lens will give a brilliant image over a yard in height which can be studied in the greatest detail hour after hour, and usually also from day to day, if necessary. The more minute movements usually become well defined after the film has thinned to four or five contrasted bands. There appear all over the film minute separate spots, circular as a rule, but of various thicknesses (as shown by their colours), and seen clearly separate on the graded colours of the rest of the film. Each moves quietly towards the region of equal colour (thickness), and finally becomes merged therein. Since the discs appear indifferently all over, it follows that some are moving up and some down. A certain aggregation usually occurs so that streams of connected discs are formed, which tend to sort themselves in order of thickness. Canals are thus formed in the film, and such continuous channels once formed often attract the wandering discs of all colours in their neighbourhood to form both ascending and descending streams—ascending in the centre and descending on each side. When such streams collide they behave as elastic liquid threads, one that is heavier or more rapid distorting or even rupturing one that is thin or slow. The separated threads then draw in to form one or more clots, or break up into many droplets, according to the circum-

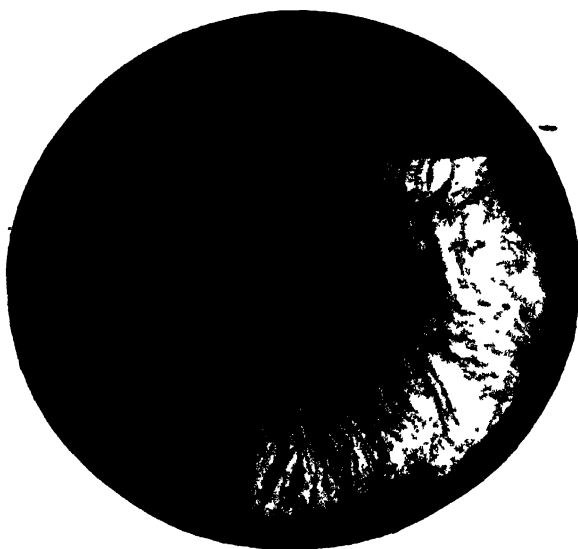


FIG. 8.

Thin black clots coalescing and rising through canals to form the black zone,
while coloured discs aggregate and fall.

(a) Early stage.

(b) Few minutes later.

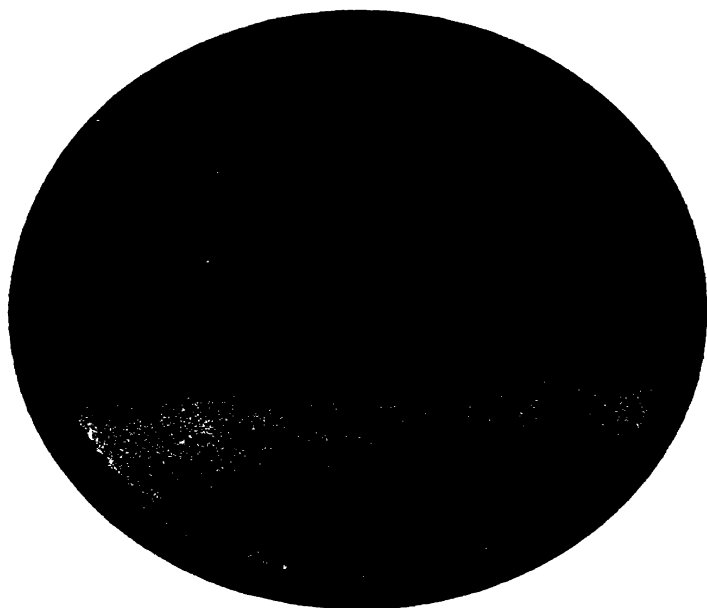


FIG. 9.

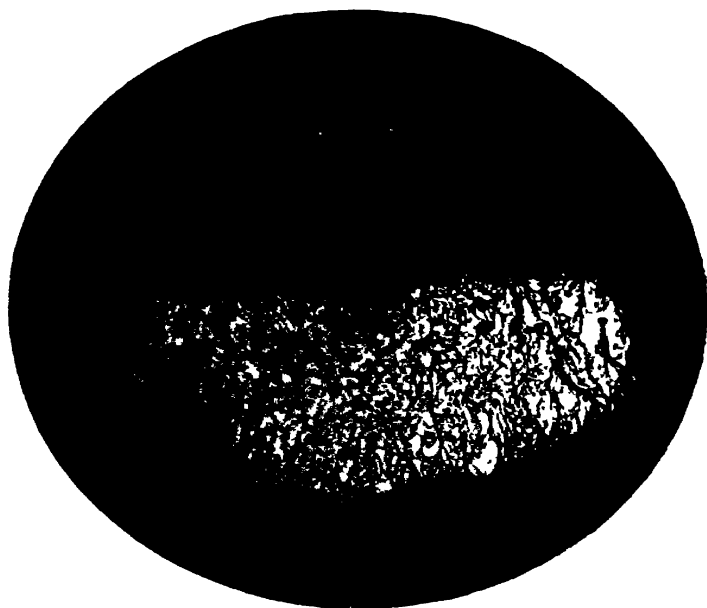


FIG. 10.

stances following the impact. Frequently two or more streams coalesce into a network or delta of frequently changing path, when the action is energetic. Fig. 8 shows these conditions.

What may be described as the sea into which such deltas discharge is the well-known black film—the thinnest portion. This is formed by the aggregation of black discs rising from all over the film. Such discs never aggregate with others of various thickness, as do those that are coloured, but pursue an independent path, for preference up the centre of the canals already described. Their movement is always far more rapid than that of the coloured material, apparently because they are relatively much more buoyant than their surroundings at the point of separation. The centre of the canals is thus frequently composed entirely of a continuous black stream; the black clots often aggregate to considerable size before being gathered into one of the streams, and then bulge the banks as they rapidly force their way through. The impetuosity is frequently such that on coming to a bend in the stream the black mass bursts the banks to form either a new stream or a new connection to a neighbouring stream.

The development may, however, vary enormously in rate, from an almost imperceptible rising of isolated tiny circles (Fig. 9) to a tumultuous aggregation of rapidly growing clots through broken canals (Fig. 10).

CRITICAL DEVELOPMENT.

A noteworthy fact is that in succeeding periods two widely different types of blackening occur in the same film, of course at very different rates. Thus in many cases, after several minutes of quiet uniform extension of the black area, a "critical" development suddenly ensues, as in Fig. 10, when with varying degrees of tumult in different cases the black area spreads practically over the whole film. This can also occur without any appreciable delay in a film still thick and banded. Fig. 11 is an example of this. The appearance is most striking. After some experiments a certain amount of control was found to be possible. A small difference of ammonia tension in the film solution from that in the neighbouring atmosphere will cause the "critical" blackening; and the tendency is either prevented or reversed by small measured variations in the amount of ammonia in the solution. Critical blackening may occur in ammonium oleate films when the ammonia present is considerably less than the quantity chemically equivalent to the oleic acid.

A solution of 6 per cent. ammonium oleate in 66 per cent. glycerin that had just become too deficient in ammonia to give the critical black fall was found (by Nesslerising) to contain 0.00030 grm. of ammonia per cc., as compared with 0.00385 grm. for "neutral." After bubbling in air and ammonia to produce strong

critical development there was still only 0·00040 grm. of ammonia per cc., the solution being then feebly opalescent. Similar values for a 0·5 per cent. ammonium oleate in 5 per cent. glycerin were 0·00007 grm. at first (slow blackening) and 0·000076 grm. after exposure to dilute ammonia atmosphere to induce the "critical" fall, as compared with 0·00032 grm. of ammonia per cc. for "neutral."

With the ammonia reduced by pure air current to 0·00025 grm. for the concentrated and to 0·00005 grm. for the dilute solution, good workable films were still readily obtained. This is in accord



FIG. 11.

with the experience that stable workable films are most safely obtained from solutions containing an excess of oleic acid.

Many measurements were made of loss of ammonia by exhaust at different temperatures, with study of the properties of the resulting solutions.

With very dilute sodium oleate solutions, a lack of uniformity of water vapour tension in the surrounding atmosphere seemed to be the cause of critical development. Thus the same solution, with the same ring support, etc., strictly employed, gave quiet steady blackening in a small closed bell jar, undisturbed by temperature fluctuations,



FIG. 12.



FIG. 13.

while when it was placed in the 1-ft. cubical glass box, containing only a small amount of the same soap solution in a shallow dish, a critical blackening ensued in almost every case after the film had been raised a few minutes. Convection currents produced in the film itself by exposure in the lamp beam (despite a large water cell) were also a disturbing cause tending to induce critical blackening and diminish the permanence of the films. A reduction in the intensity and extent of the critical development followed when the atmosphere of the cube was more fully saturated with water vapour. The largest number of grades of black and silvery colour were obtained under these conditions; misty black films separated into deeper black areas of different intensity, usually circular in shape when first formed, and surrounded with a "necklace" of glittering silvery beads due to the aggregation of the half-black layers from the deep black areas. Later, curious nebular drifts of grey or silvery discs of all sizes were formed by the convection resulting from exposure to the lamp beam. Figs. 12 and 13 are examples.

With tri-ethylamine solutions the critical stage could be readily brought about by carefully introducing small quantities of tri-ethylamine vapour into the cube, a slow current of air bubbled through a few cc. of tri-ethylamine being sufficient. Pure air, to remove the excess of base, again stabilised the films and reproduced a steady development.

The addition of uranin—up to a proportion equal to that of the soap—usually produced the most tumultuous critical development of all, though some samples of purified oleic acid did not give these results.

In general the black films resulting from a critical development did not last long, and in the most violent productions the film burst as a rule before becoming completely black, or a very few minutes after.

In most cases the extent of the critical development could be controlled by varying the amount of excess liquid that was allowed to remain at the bottom of the ring. For example, in one case, when only one or two drops of the excess liquid were drained off after raising the film, the black developed quietly half-way down before breaking out into the critical tumult. When five or six drops of the excess liquid were removed, only one-third of quiet development occurred before the critical stage. If the initial drainage were almost complete (7 to 10 drops), the critical stage ensued almost at once, before more than 5 per cent. or 10 per cent. of quietly formed black had appeared. With some solutions the critical development could also be broken into two or three stages with intervals of quieter development by successive momentary applications of the draining wires; this occurred on one occasion with a film from a solution of 0.5 per cent. ammonium oleate in 5 per cent. glycerin, which went quietly to one-third black and two-thirds mainly silvery in less than three

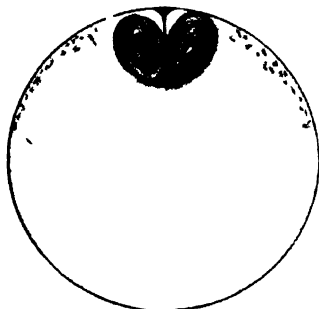
minutes. Then the critical fall occurred, and in $1\frac{1}{2}$ minute further had produced 80 per cent. black, leaving 20 per cent. silvery to blue which re-aggregated and developed quietly as at the start, but took 15 minutes more to become all black. If, however, the drainage wires were touched on the bottom of the ring to remove the excess liquid that had accumulated, the tumultuous black production was again seen, and in less than two minutes only a streak of silvery film was left below.

The most active solution for tumultuous blackening of those containing a proportion of uranin equal to that of the soap had 2 per cent. each of ammonium oleate and uranin in 20 per cent. glycerin. A film from such a solution frequently took only 10 seconds to become completely black, after remaining for three or four minutes quietly thinning to a succession of the usual colour bands with very little black (Fig. 8).

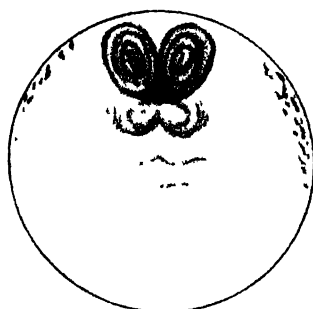
This sudden development is often readily stimulated by a gentle stream of pure air at about $\frac{1}{2}$ cm. of water pressure through a glass tube constricted to a nozzle of less than 1 mm. Such tubes are shown in Fig. 4 above and below the film ring, bent over to direct the jet upon the film at a moderate inclination. A jet from the top is the most effective in stimulating the rapid development. The thin colour bands formed in the initial stages then aggregate into thick colourless clots, broken and scattered by the tumult, and crowd down into a small area or even a few drops. The action was found to occur whether the film was illuminated for projection or was in a dark room with only a dim lamp at a distance to give enough light to show what was taking place. Ten successive films gave the same result. However, when the solution was gradually deprived of ammonia by a regulated air current through the cube, it became unstable, so that more and more jet stimulation was necessary to produce the critical black fall.

With 5 per cent. ammonium oleate in 50 per cent. glycerin, a film on a wire frame 11 cm. square developed as follows:—The ammonia present had been reduced so that the critical blackening would not occur without jet stimulus. Twenty minutes after the first separation of black a zone $1\frac{1}{2}$ cm. deep had formed. One thin canal was present in the centre of the coloured portion, through which the circular black clots ascended rapidly from time to time, while on the boundaries of the canal there were continuous up-and-down convections of coloured cell-like clots (direction according to colour). Five minutes later two such canals had formed, and in 20 minutes there were four interconnected near the centre as well as a delta network of 8 or 10 other canals towards one side. (Similar formations can be seen in Fig. 8.) A jet of air through a 0.3 mm. nozzle was then directed upon the film a little below the black boundary. The resulting streams and vortices mixed the black in large clots through the coloured area. The jet was kept on for half a minute

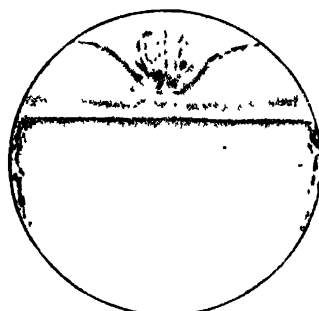
FIG 14a.—CONCENTRATED SOAP.



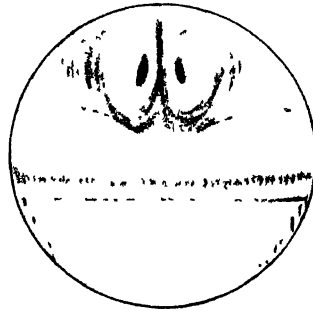
(1)— $\frac{1}{2}$ min



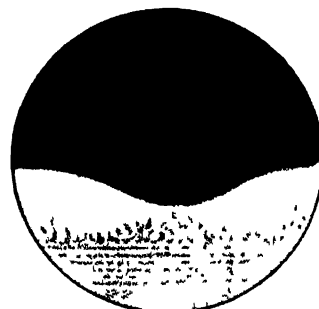
(2) - $1\frac{1}{2}$ min



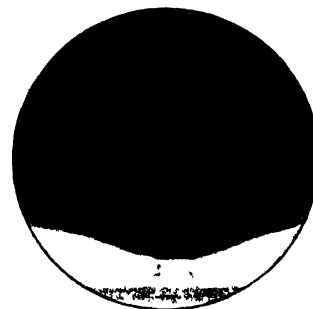
(3)—10 min.



(4) 22 $\frac{1}{2}$ min.

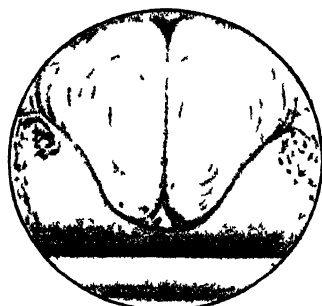
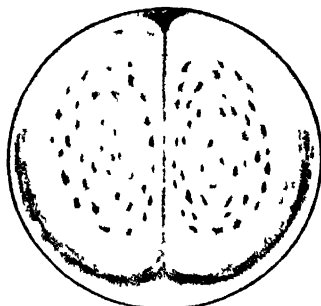


(5) 30 min.

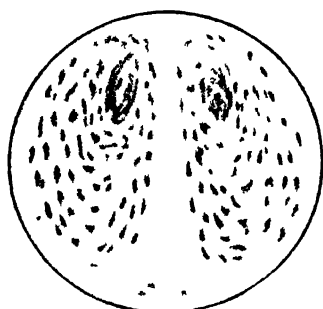


(6) -40 min.

Air jet from top 3 mm. water pressure.

FIG. 14*b*.—DILUTE SOAP(1)— $\frac{1}{4}$ min

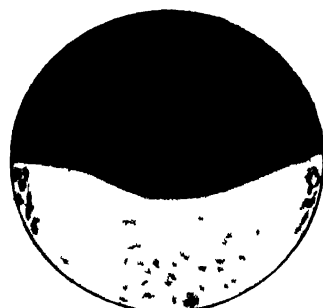
(2)—5 min



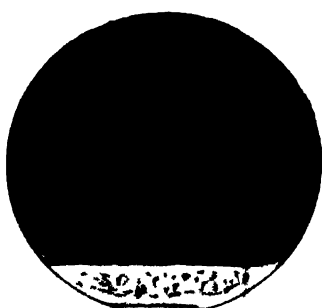
(3)—12 min



(4)—18 min



(5)—24 min



(6)—45 min

Air jet from top 3 mm water pressure

only. Blackening then proceeded rapidly by a multiplication of canals which soon became a violent tornado of black waterspouts through the silvery and coloured region. This subsided in five minutes with only about 1 cm. of coloured film remaining below the black.

These rapidly developed blacks were the deepest of any obtained with soap solutions containing glycerin, as were mostly employed, because they were more easily stabilised. But in the few cases in which the glycerin was reduced in amount or left out, there was frequently very active (though not tumultuous) development to an extremely deep "velvety" black, with ready differentiation of silvery grades on the black. This especially characterised the more dilute solutions *e.g.* of the order of 0.5 per cent. of oleate. Excess of oleic acid is then to be avoided as it reduces the mobility.

SLOWER DEVELOPMENT.

The more usual development is quite slow, taking perhaps one hour for the black to extend through an $8\frac{1}{2}$ cm. film. The relative thicknesses and densities of the coloured bands are then very strikingly shown by the relative vigour of the vortex streams produced in different parts of the film by a quiet maintained jet of air through a small nozzle. When the film is freshly raised and thick enough to exhibit about 15 or 20 bands, a tiny vortex only is produced by a jet of 5 mm. water pressure through a glass nozzle 0.3 mm. diameter inclined at about 20° to the film and distant 2 mm. As the thinning progresses, the same jet produces a larger and larger vortex, which has extended over practically the whole width of the film by the time the silvery to golden stage is reached and black spots are beginning to separate. These are then drawn into a vortex on each side of the central straight stream, slowly coalescing into a steadily growing continuous black elliptical area and leaving a thinner and thinner central silvery or faintly coloured stream that circulates as a coloured fountain round the periphery and again into the thin central stream. The black extends steadily until only the dainty silvery or faintly coloured stream persists along the centre. This gradually disappears, but leaves an indentation in the sharply defined boundary separating the black and coloured areas. This indentation grows steadily flatter as the black boundary recedes from the jet above, until when the film is about 90 per cent. black only a small central curve is left.

Some of the successive stages are shown in *Fig. 14a* and *b* (pp. 18, 19). *Fig. 15* is a photograph taken when there is still a silvery stream across the black; the vestiges of the outer circulation of the complete

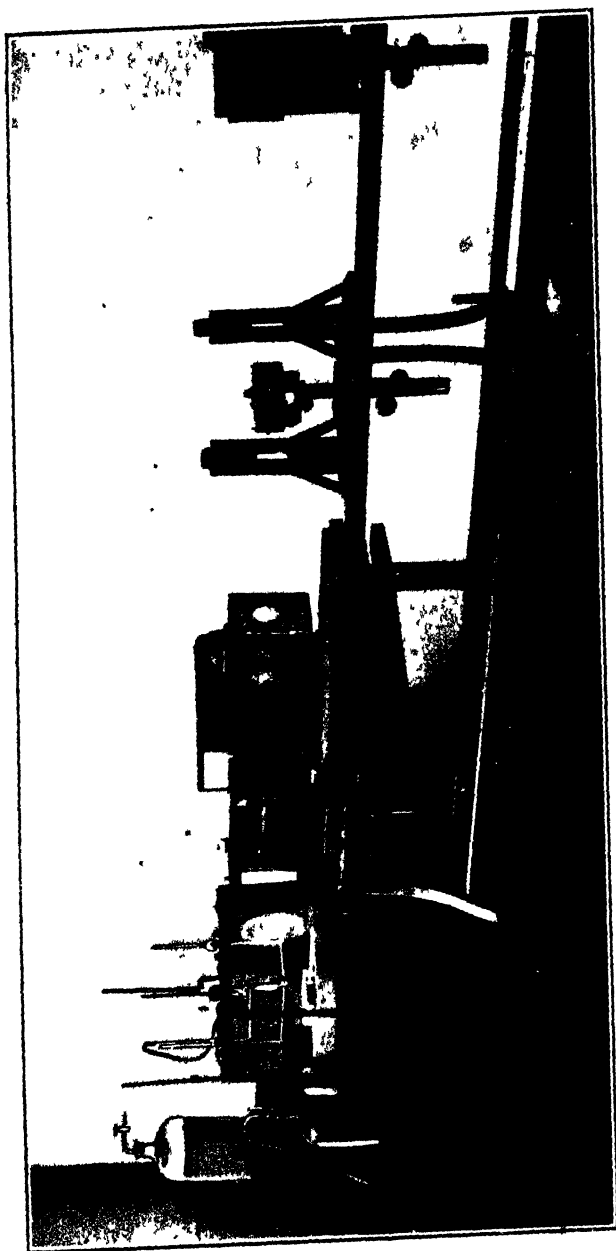


FIG 17.

produced by jets at higher pressure when directed from below (*i.e.* the thick end of the film) at glancing incidence, in which case they increase in size away from the jet, which is the direction in which the film thins out, the final coloured vortex being projected well into the black when this separates. These and any other quiet formations are readily sketched, when required for subsequent study, on transparent paper fixed in place of the ground-glass screen in the camera arranged to receive the projected image.

The relative intensity of illumination of different parts of the film and of various grades of black was measured with the camera at one end of a 3-metre optical bench, carrying also a photometer on a sliding carriage and a standard illumination formed by a sheet of semi-transparent paper on an opening in a box also sliding on the same photometer bench and enclosing a 60-watt lamp. The arrangement is shown in Figs. 16 and 17. The image of a half-black, half-silvery film can be seen in Fig. 17 focussed on the camera ground glass. Such images were screened as desired to compare the illumination of any part.

Some of the typical values obtained are given in Table I., though these measurements do not include the deepest blacks, *e.g.* those from very dilute soap solutions without glycerin. The values represent the relative luminous intensity of the whole film area—approximately 50 sq. cm.—and are in terms of the steady uniform source of light employed—*viz.* the window of the 60-watt lamp box, of the same area as the film, and covered by a translucent paper screen. The positions of the camera and light source were fixed, while the photometer was adjusted to a match for the various film images. In every case the films were illuminated by the same arrangement of 1000 c.p. Pointolite lamp and condenser and water cell.

The figures indicate several definite increments of black luminosity, and presumably therefore of thickness. Thus (4) bears to (5) the same relation as (6) does to (10), although the values relate to different solutions. Also (2) bears to (1) twice the ratios of (5) to (4) and (10) to (6). So also the values found for the thicker blacks noted at (2) and (8) are very nearly simple integral gradations from the others, if the silvery film is taken as the standard for each solution, *e.g.* :—

$$\begin{aligned}(1) : (2) : (3) &:: 26 : 4 : 3 \\(4) : (5) &:: 26 : 2 \\(6) : (8) : (10) &:: 26 : 7 : 2\end{aligned}$$

Perrin distinguished 18 thicknesses of black-grey and white, and suggested that the films were "stratified" and composed of equal layers or leaflets. P. V. Wells,† continuing this study, found all these

* *Ann. de Ch. et de Phys.*, 1918, x, p. 160.

† *Ann. de Ch. et de Phys.*, 1921, xvi, p. 69.

layers to be of equal thickness, viz. $4.5 \mu\mu$, which would correspond to a bi-molecular film in accordance with the calculations and measurements of oil films on water.

TABLE I.—RELATIVE LUMINOUS INTENSITIES OF DIFFERENT REGIONS OF THE FILM.

	Terms of Light Source	Other Relations
I. VISCOUS PLAQUE SOLUTION.		
(1) Uniform silvery film	2.34	
(2) „ slowly developed black...	0.355	$\frac{1}{6.60}$ of silvery
(3) „ black; after several hours, settling of misty haze	0.280	$\frac{1}{8.11}$ „
II. SAME SOLUTION RENDERED CLEAR AND MOBILE (BY AMMONIA).		
(4) Uniform silvery film	1.853	—
(5) „ steadily developed black	0.141	$\frac{1}{13.14}$ of silvery
III. $3\frac{1}{2}$ PER CENT. AMMONIUM OLEATE IN 33 PER CENT. GLYCERIN.		
(6) Silvery film	2.19	—
(7) Unthinned (colourless) film ...	2.37	—
(8) Grey-black; hazy	0.578	$\frac{1}{3.8}$ of silvery
(9) *Deep “critical” black with 8 per cent. silvery	0.118	—
(10) Uniformly quietly formed black ...	0.166	$\frac{1}{13.2}$ of silvery
(11) Silvery to blue film	1.115	—
(12) 54 per cent. silvery, 46 per cent., medium black	1.18	—
(13) † 54 per cent. silvery aggregated by slow motion by low pressure jet	0.444	0.24 of silvery

* Almost all this light is referable to the small silvery zone showing that the deepest “critical” black reflects a negligible amount—approximately 0.08 of the light source, or $\frac{1}{12.5}$ th of the silvery.

† The proportional reflecting area of silvery is thus reduced from 54 per cent. to 20.4 per cent.; which is the aggregation into spheres caused by the motion

Some interesting phenomena were noticed in connection with the viscous tendency of some solutions already alluded to, which is apt to prevent the formation of real deep black.

The first instance was that of some old “Plateau” solution (3 per cent. sodium oleate in 30 per cent. glycerin approximately), prepared

some six years previously from "pure" sodium oleate. On three occasions it had been carefully separated from a thin layer of ropy scum that had risen. The clear solution gave extremely stable films lasting over a week with a jet of pure air directed at glancing incidence from a $\frac{1}{4}$ mm. glass nozzle. Some turbidity was meanwhile formed in the solution (in a dish in the film cube, Fig. 4); and on stopping the air jet, the film developed to black in the usual way.

On several occasions after the films had remained undisturbed all night (in the dark room where the work was done), a curious formation of silvery discs and streaks was observed. Figs. 18 and 19 are reproductions of photographs of these—reminiscent in some cases of the Martian canal formations. They were formed by the slow convective motion of silvery discs in the viscous black film, no doubt induced by slow local temperature changes through the night, as by exposure of one side of the film cube to a small continuous draught from door to ventilator. The circular silvery tracks very definitely separated zones of different grades of black on the film. The sluggishness and turbidity were rectified by adding a single drop of 3 per cent. ammonia to the solution, the effect, however, being only transitory when any gentle air current was maintained through the cube. Small additions of tri-ethylamine had a similar but much more lasting effect.

Another instance was the production of a streaky viscous black zone in some 20 cm. bubbles blown from solutions of ammonium oleate in dilute glycerin prepared from some oleic acid which had been carefully purified in the laboratory, and which gave an almost theoretical iodine number. Moreover the black had in many of these cases been produced by a "critical," or at any rate very rapid, fall, and thus came from a mobile solution. In contrast to this was a deep and mobile black produced from a solution prepared from some oleic acid that had been distilled (above 100° C.) in a charcoal vacuum, and thereby had its iodine number reduced from 90 to 40. Apparently it had been partially transformed to saturated acid, and thus would be expected to give a more viscous black than the purer oleic. On the contrary, however, the first streaky solution gave distorted silvery markings, with hardly any of the mobile convection (of silvery discs, etc.) which is seen in a normal black film, and which was visible in the solution prepared from the distilled acid.

There is of course the effect of the glycerin admixture to be considered. A direct case of the action of glycerin in preserving the mobility of black films was met in the course of extensive measurements of the rate of fall of black drained soap films in long exhausted tubes. When a small proportion of glycerin was present the films fell continuously; but with pure soap the fall was arrested in a few days, and the film became apparently "gelatinised" and set to one position. When it broke it left a permanent viscous ring on the tube, easily soluble however in the bulk of the solution in the tube.

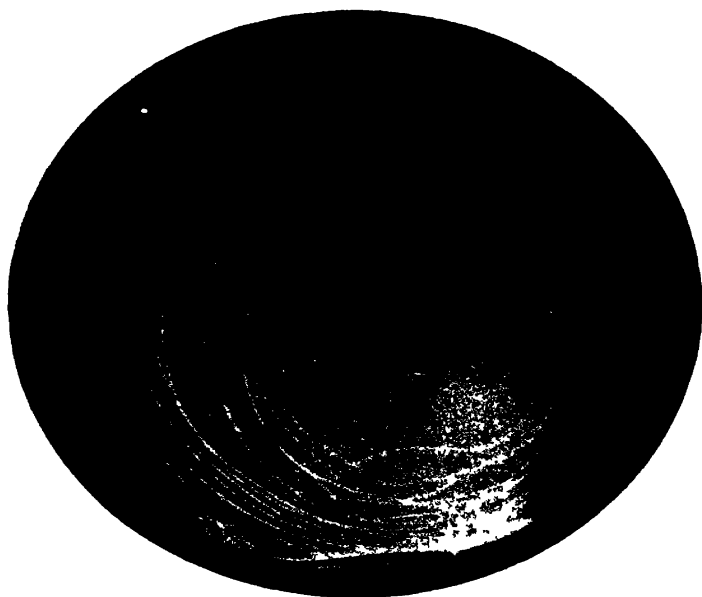


FIG 18.

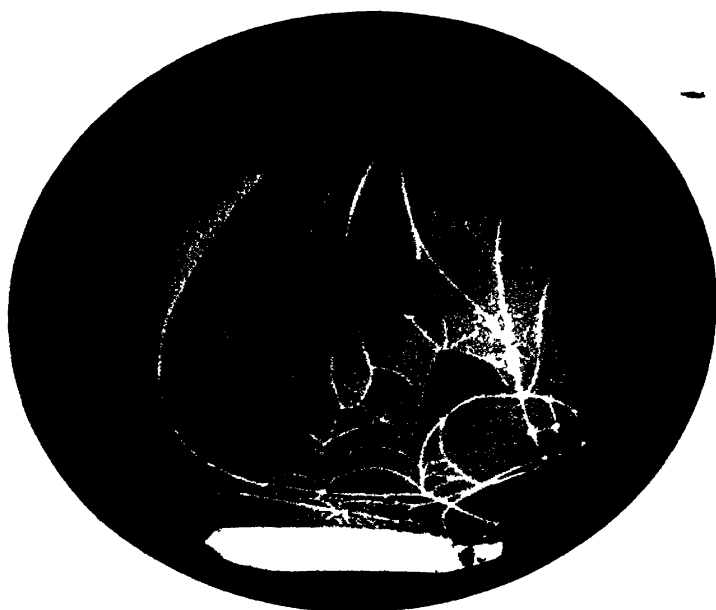


FIG. 19.

FORMATION OF NOZZLES.

Many convenient nozzles for the film jets were made by piercing small discs of platinum foil, which were then readily sealed on the smoothed ends of glass tubes. These could be bent at any required inclination, so that while the glass tube could slide vertically in a gland in the top of the film cube, the actual jet could impinge at any required inclination. The holes in the foil were not carefully burnished for most purposes, but were made by placing the disc on a smooth clean piece of lead, and placing on it a small cork in which was embedded a piece of needle of the required thickness with its point just evident through the cork. A light smart blow with a hammer then gave a suitable nozzle; from several such the best were selected after examination and trial.

Glass nozzles were made by drawing out glass tubing to the shape desired, the constricted part being generally as short as possible. Strictly circular holes were not so easily made in this way, but the deviation seemed sometimes to be an advantage for producing a responsive jet.

The resulting orifices were measured under the microscope for the purpose of determining the jet velocities, etc. For jets at anything like normal incidence the pierced foil discs were preferred; while for those at glancing or inclined incidence the glass nozzles were more easily adapted.

The production of a fairly high speed jet by a small increase of pressure may be demonstrated by the apparatus shown in Fig. 20. An ordinary boiling flask of about $\frac{3}{4}$ of a litre capacity has a blackened annulus of cardboard fitted in the centre of the bulb, with its plane in the axis of the neck. A small iron gauze capsule containing fresh soda-lime granules is fitted tightly into the neck, which is then sealed off. To the side tube is sealed a three-branch Regnault stopcock, the outward horizontal branch being closed by a sealed-on disc of platinum foil pierced by a needle with a single $\frac{1}{2}$ mm. hole. The remaining vertical branch can be opened to equilibrate the pressure in the flask to that of the atmosphere before use. The pierced platinum foil jet is protected in a blackened box with glass sides which are inclined off the vertical to obviate hazy reflections. A light paper or pith square is held by a bifilar silk suspension just clear of the hole in the foil, an adjustable sliding cap being provided for this purpose in the top of the protective box. When a parallel horizontal beam from the arc is projected through the bulb of the flask, the black annulus absorbs some of the heat and communicates it to the air in the flask, which thus expands and forces a tiny jet out through the hole in the platinum foil, the paper target being thereby displaced. By means of a small mirror (not

shown) in a vertical plane at 45° to the beam, the jet is illuminated in a perpendicular direction and focussed by a lens on the other side upon the screen parallel to which the arc lamp beam is projected. A glass water cell is placed in the path of the beam while the projection is focussed, and the paper target is then seen hanging quietly at the platinum orifice. On removing the water cell, and thus allowing the heat rays to pass, the bulb warms up and the paper at once swings away from the jet; after "exposing" for a few seconds in this way, the water cell is replaced and the paper square again settles back against the nozzle.

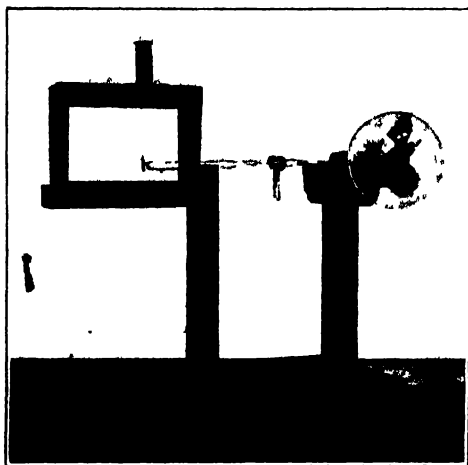


FIG. 20.

PRODUCTION OF STREAMS AND VORTICES.

A single puff by a jet directed upwards across a black film with about one-fourth remaining silvery or coloured will project a double vortex-ring section pattern outlined in silvery or colour on the black. With care the vortex does not break loose, as seen in Fig. 21, but after reaching a moderate height, as in Fig. 22, returns and contracts through such forms as those in Figs. 23 and 24 as it shrinks back from the "stretching" induced by the puff, thus giving a good illustration of the "elastic" separation of the silvery or other defined zones from the black film.

If before collapse occurs, a second puff is projected, the first is impelled forward, and so by a succession of puffs the building up of a maintained stream can be observed by a progression of rotating vortex rings. When these meet the far boundary of the film they are reflected and deviated to either side, and so pass round and are again brought into the centre near to the main stream, continuing to converge according to the limits of the film. (See for example, Figs. 25, 27*a*, 28, 31 and 35.)

When the circulation is established, the streams are often composed of separate droplets, as in Fig. 26. This is shown by photographs taken by the illumination of a spark (from four 3-litre Leyden jars charged by a Wimshurst machine) situated at the focus of a lens of 11-in. aperture and 8-in. focus close to one side of the film cube. Exposures with arc illumination of a thousandth of a second focal plane exposure (*a*) are compared in Figs. 27, 28 and 29 with the spark photographs (*b*) taken on the same vortex within one or two minutes—the time required to change the dark slide and replace the arc by the spark (already exactly arranged). One interesting case is illustrated in Fig. 30, which is a spark photograph of a film set in rapid circulation by a central jet. To the eye this appeared as a perfectly uniform grey misty film, but it is seen to be composed of streams of silvery droplets on a black film background.

Vertical and horizontal jets give fine sharp stream lines across the film with elliptical eddies on each side, usually very symmetrical except sometimes as to colour. The shape and position vary with the force of the air current and the orientation of the nozzle. A feeble jet does not give a stream line across the whole film, but a symmetrical fountain whose height and character can easily be adjusted by small alterations in pressure.

By combining a vertical and a horizontal jet quadruple vortex or eddy patterns can be obtained.

By carefully opposing two horizontal or two vertical jets (at a pressure of a few millimetres) bouncing spurts of colour in regular alternation can be obtained, or with a little more pressure the centre is divided into four symmetrically disposed brushes of colour varying with the thickness of the film.

Nozzles of pierced foil arranged to give a jet normal to the film produce a central stream line spreading out on each side into eddies shaped like butterfly wings, and these are also wonderfully simulated by the gorgeous colours that grade in bands to a central "eye" which finally becomes black.

The more viscous solutions give very long-lasting colour patterns: one or two films of ordinary "Plateau" solution ($2\frac{1}{2}$ per cent. sodium oleate in 25 per cent. glycerin) were maintained as a trial for over a week without appreciable variation. The air supply was derived from the large compression bottles of the low-temperature plant. More dilute or mobile solutions, however, go more or less rapidly



FIG. 21

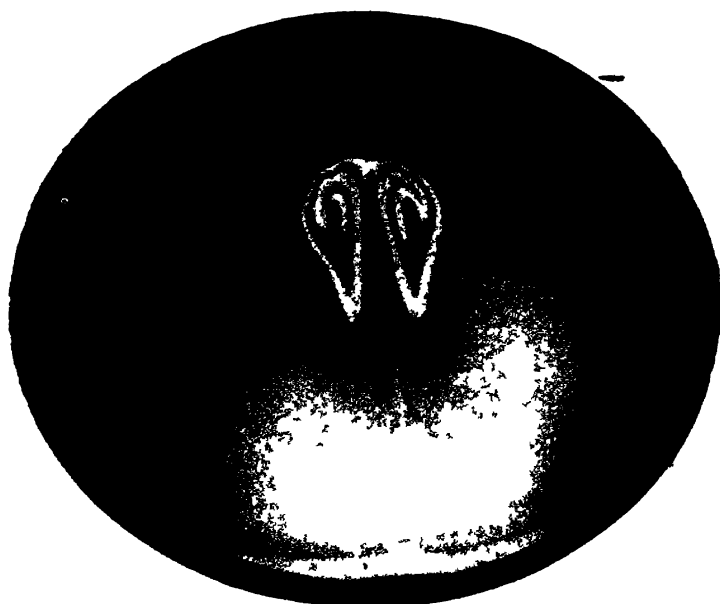


FIG. 22

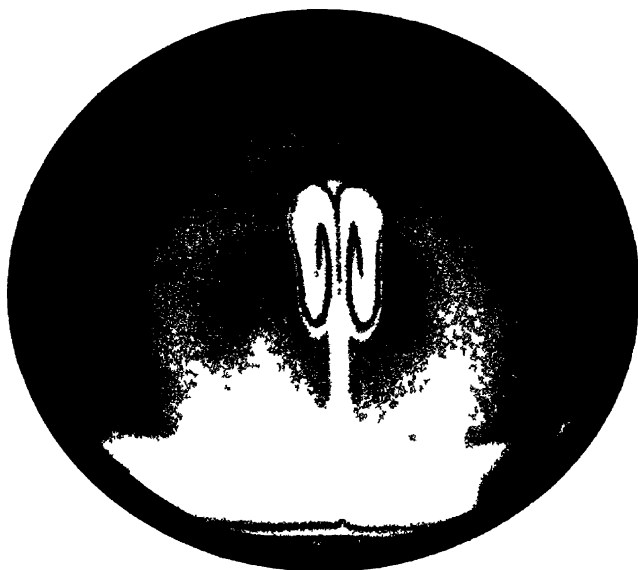


FIG 23

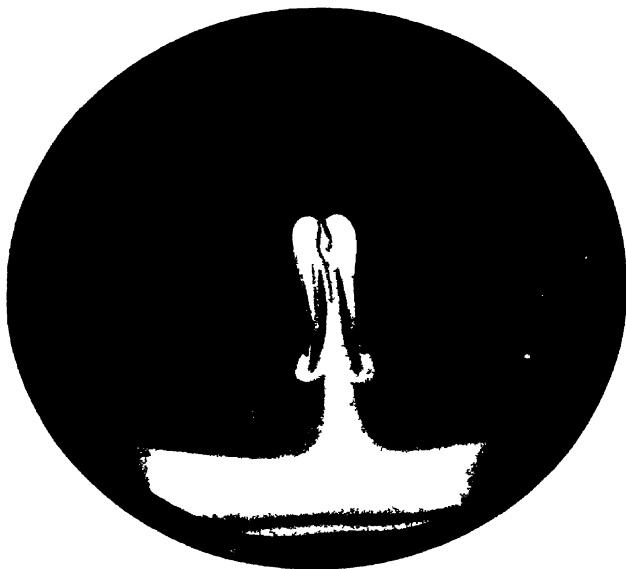
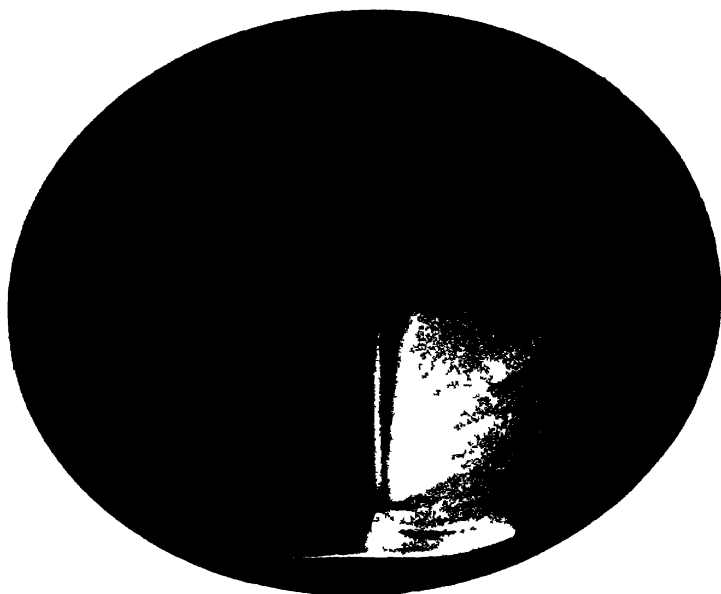
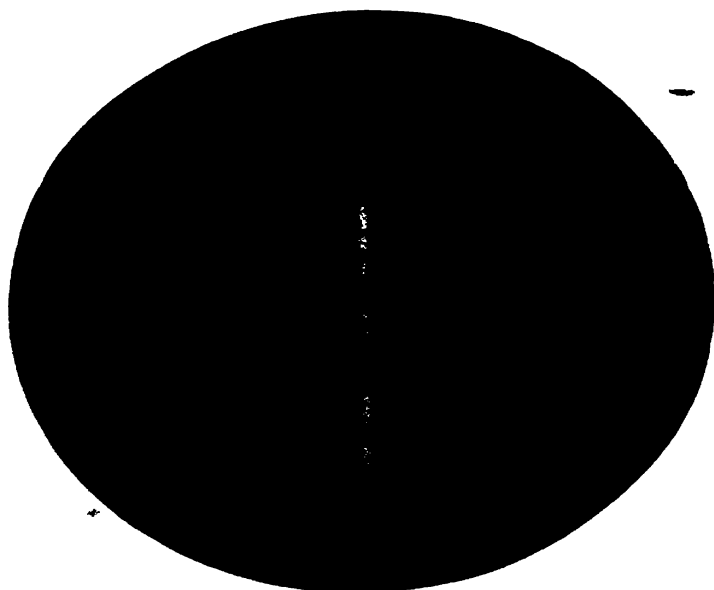


FIG 24



1/1000 sec
FIG. 25.



Spark—Same Film
FIG. 26

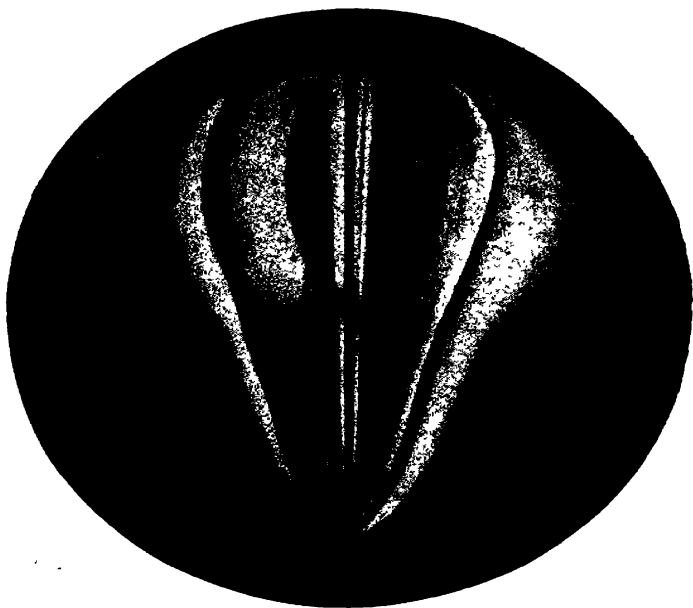


FIG. 27 (a).

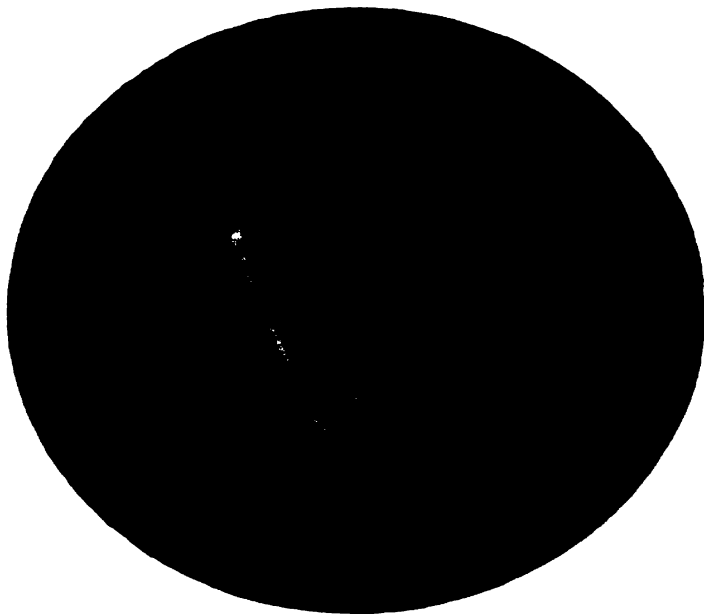


FIG. 27 (b).



FIG 28 (a)

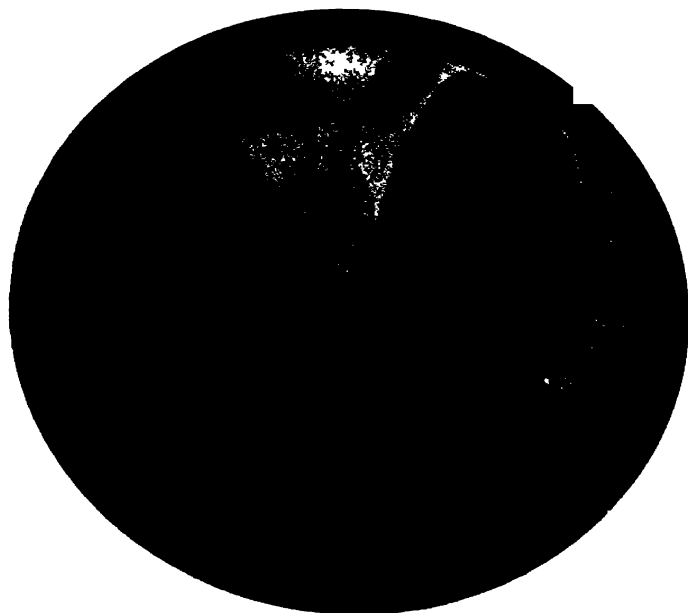


FIG 28 (b)



FIG 29 (a)

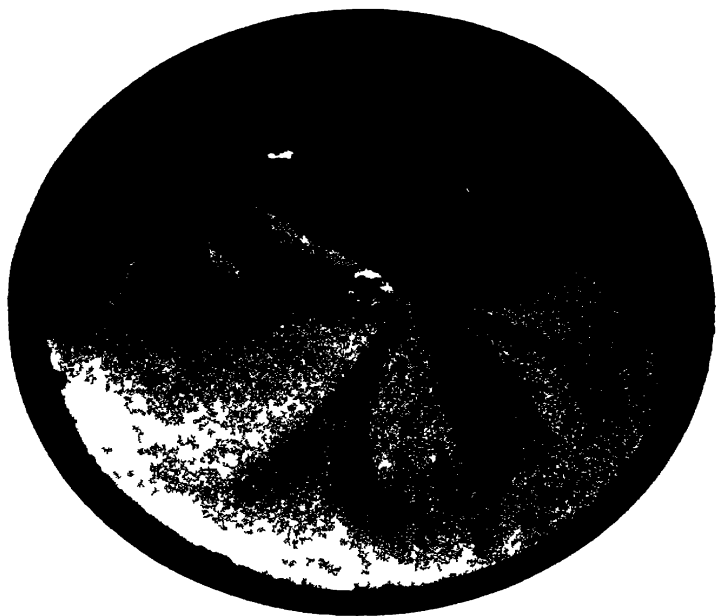


FIG 29 (b)

through the gradations of colour, until a black eye separates at the "centre" of the vortex or eddy. This of course extends while the colours retreat and fade until a silvery stream only is left over the black film. The liquid has now accumulated in the "Gibbs channel" round the film ring, with most of it in the lower portion. If an upward pointing jet is now directed into this region, more and more liquid can be fed into the stream over the black, which can be built up into splendidly coloured fountains on a black background,

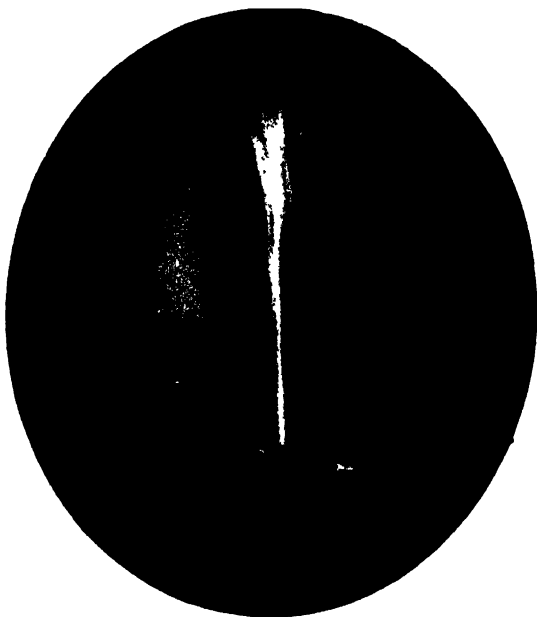


FIG. 30.

until the original coloured eddies or butterfly wings are reproduced. So also in "running" a film for some time, as described, with the normally inclined jet, if the colours fade too much, a short application of a jet, from the thicker liquid accumulations below, will feed more liquid into the eddies and build up the colours once more. Several brilliantly coloured autochrome photographs were obtained, the exposure for which with arc illumination could be as low as $1/25$ second. In all the film photographs a lens of full $3\frac{1}{2}$ -in. aperture was employed. This was an old heavy Ross lens made for

lantern projection, and was specially fitted with its own panel and support on the photometer bench in front of the camera, as seen in Figs. 16 and 17.

SOUND SENSITIVITY OF JETS.

Under certain conditions of pressure and distance from the film, nozzles of suitable shapes gave jets that were responsive to sounds of many kinds. The response was most strikingly shown by a transformation of the pattern made on the film by the undisturbed jet. On measuring the velocities through the jets and noting the rate of streaming motion, etc., in the film, it became evident that the rate of transmission of the disturbance was considerably reduced by being impressed on the film, and its character could thus be more readily followed. Photographs taken with the exposure of an ordinary focal plane shutter then sufficed to record the perturbation on the normal straight stream lines. Examples are shown in Figs. 31, 32, 33 and 34. Fig. 31 shows the undisturbed stream line; Fig. 32 the disturbance from a "clicker" (lecturer's slide signal); Fig. 33 from "Oh" sound sung to middle C; and Fig. 34 from a cab whistle (single blast). In Fig. 35 there is a steady stream from the air jet at nearly normal incidence through a pierced platinum foil nozzle opposite the centre of the film, and in Fig. 36 it is disturbed by a whistle. Figs. 37 and 38 are a similar pair, but there is only a single short pulse from the whistle, which appears as a single distortion near the end of the radial stream line in Fig. 38. Figs. 39 and 40 are spark photographs in which a steady streaming film is compared with the stationary ripples produced by continuous whistling. In Figs. 41 and 42 the jet is on the point of "flaring" (comparable to singing flame); in the former there is no sound, but the latter is disturbed, as by whistle, voice, clicker, rustling of paper, etc.

JET VELOCITIES.

The measurement of the jet velocities was made by noting the volume delivered in observed times, at certain constant pressures. Aspirators of from one to five litres capacity were fitted as Mariotte bottles to deliver at constant pressure,* regulated through a screw cone spindle valve and registered close to the jet by a water manometer. The growth of velocity with pressure was thus determined; some of the curves representing this in certain cases with air, hydrogen, and

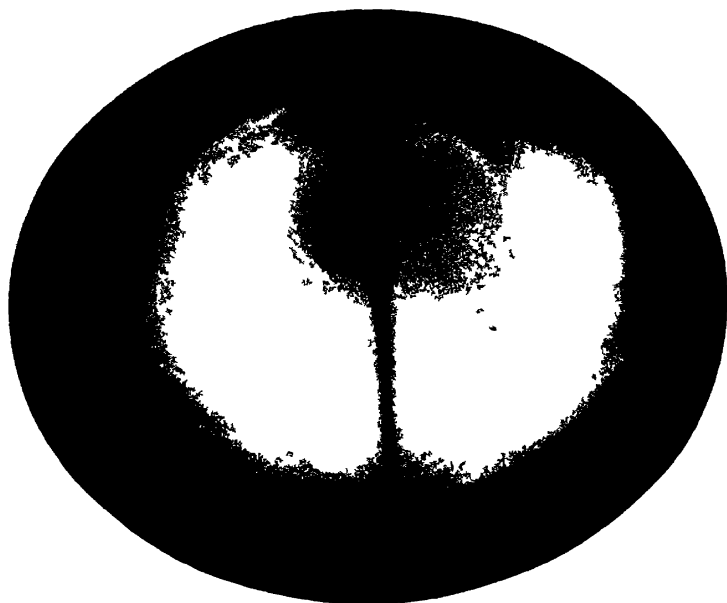


FIG 31.



FIG 32.

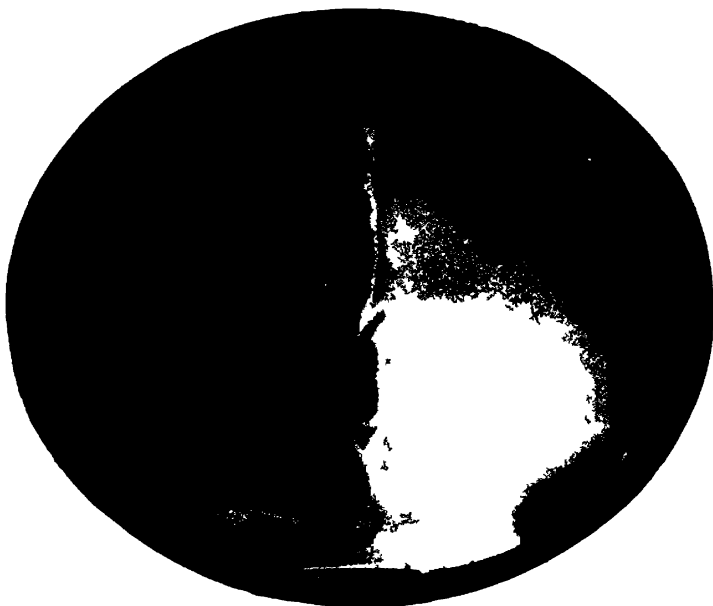


FIG 33

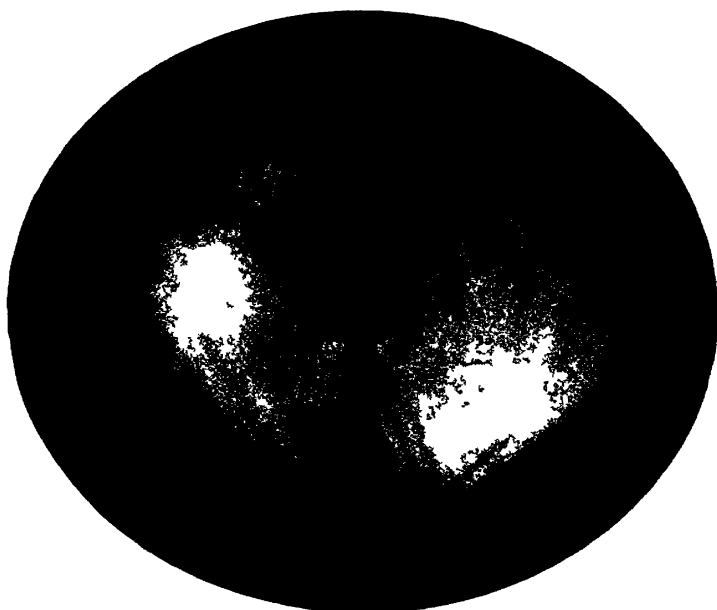


FIG. 34

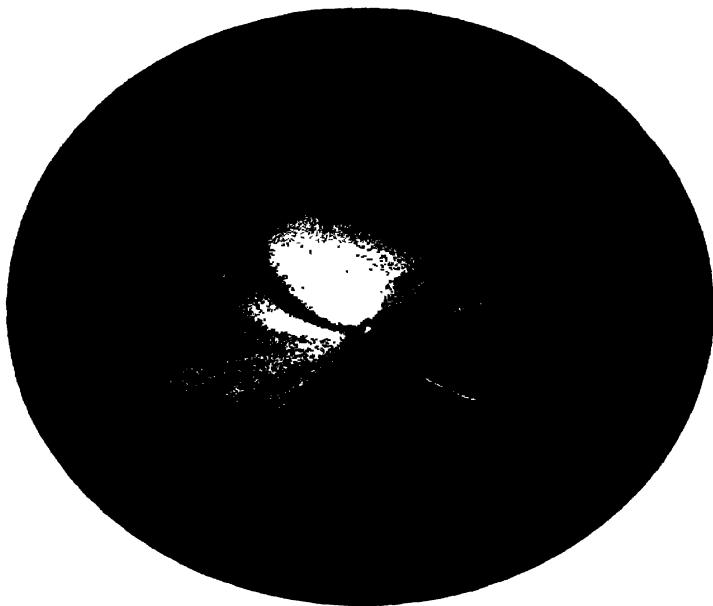


FIG. 35.

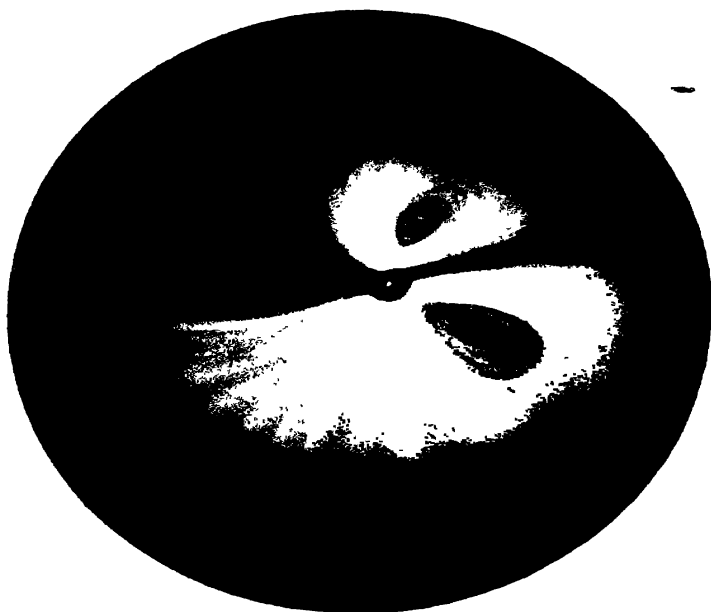


FIG. 36.



FIG. 37.



FIG. 38.



FIG. 39

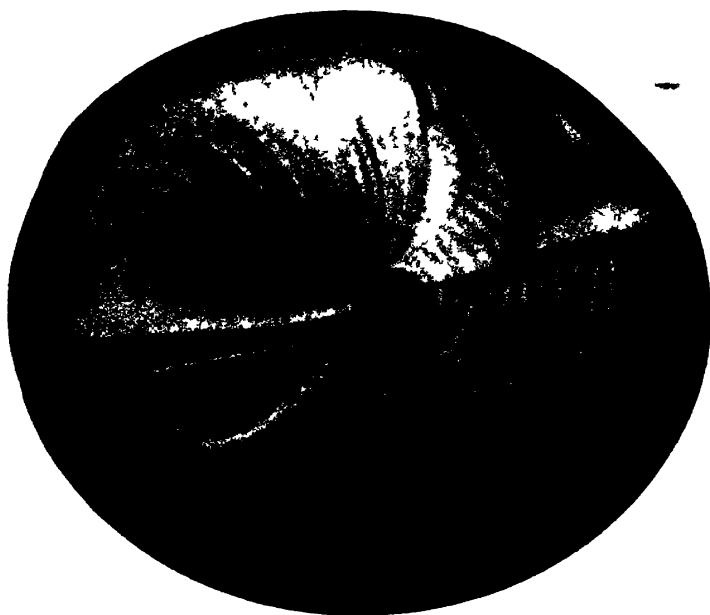


FIG. 40.

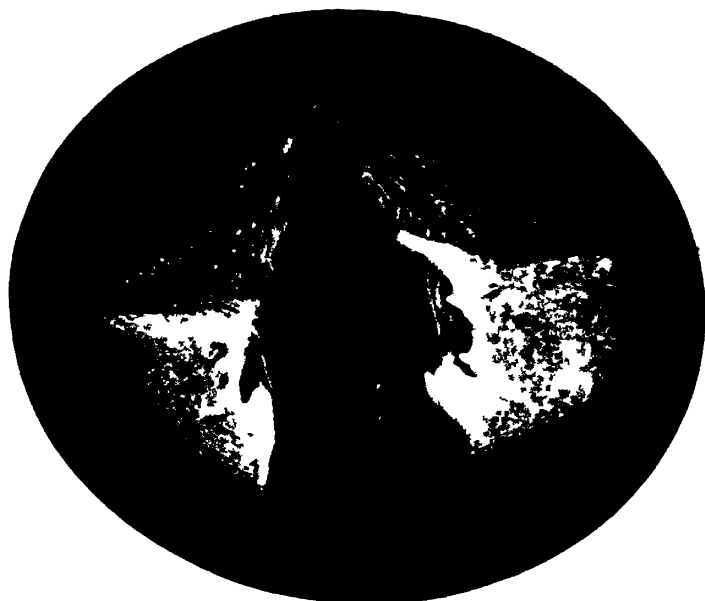


FIG. 41



FIG. 42.

nitrous oxide are given in Fig. 43, which also includes a curve computed from the results of recent experiments by Thomas.* The values for air, nitrous oxide and hydrogen are also given in Table II.

The relation between the plus pressure, to produce a jet through a small hole in a thin diaphragm, and the speed of the gas through the hole was given by Dupré as $V^2 = K \frac{T}{D} \log \frac{p_1}{p_2}$, where $\frac{p_1}{p_2}$ is the ratio of pressure (in atmospheres) on the two sides of the orifice, and T and D are temperature and mean density, K being a constant for

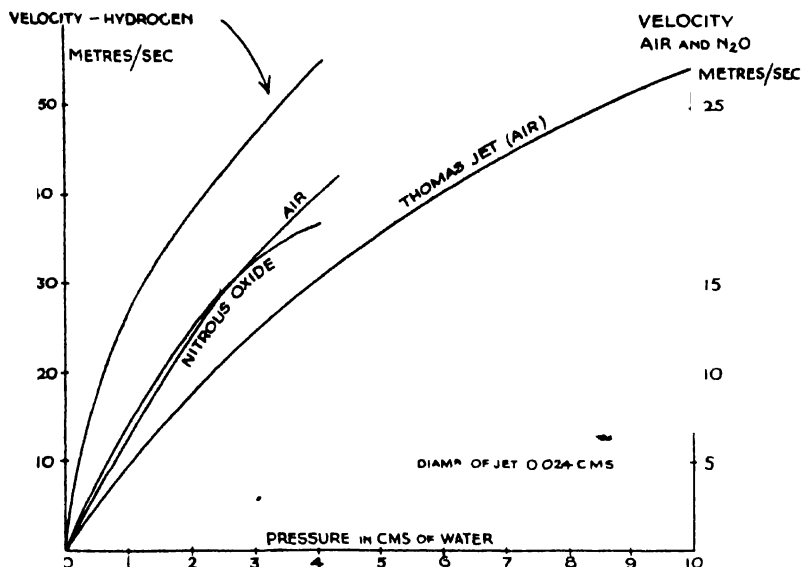


FIG. 43.

the jet. Fig. 44 shows the manner of the variation of velocity with pressure ratio and log pressure ratio respectively, calculated from this expression. Included also are computations on a similar basis of some of Thomas's results.

Values obtained with various jets are as follows:—The variation is generally regular up to the point at which the jet "flares," which is always shown by a violent commotion on the soap film, quite comparable to the well-known appearance in a Tyndall singing flame.

* *Phil. Mag.*, Nov. 1922, p. 975.

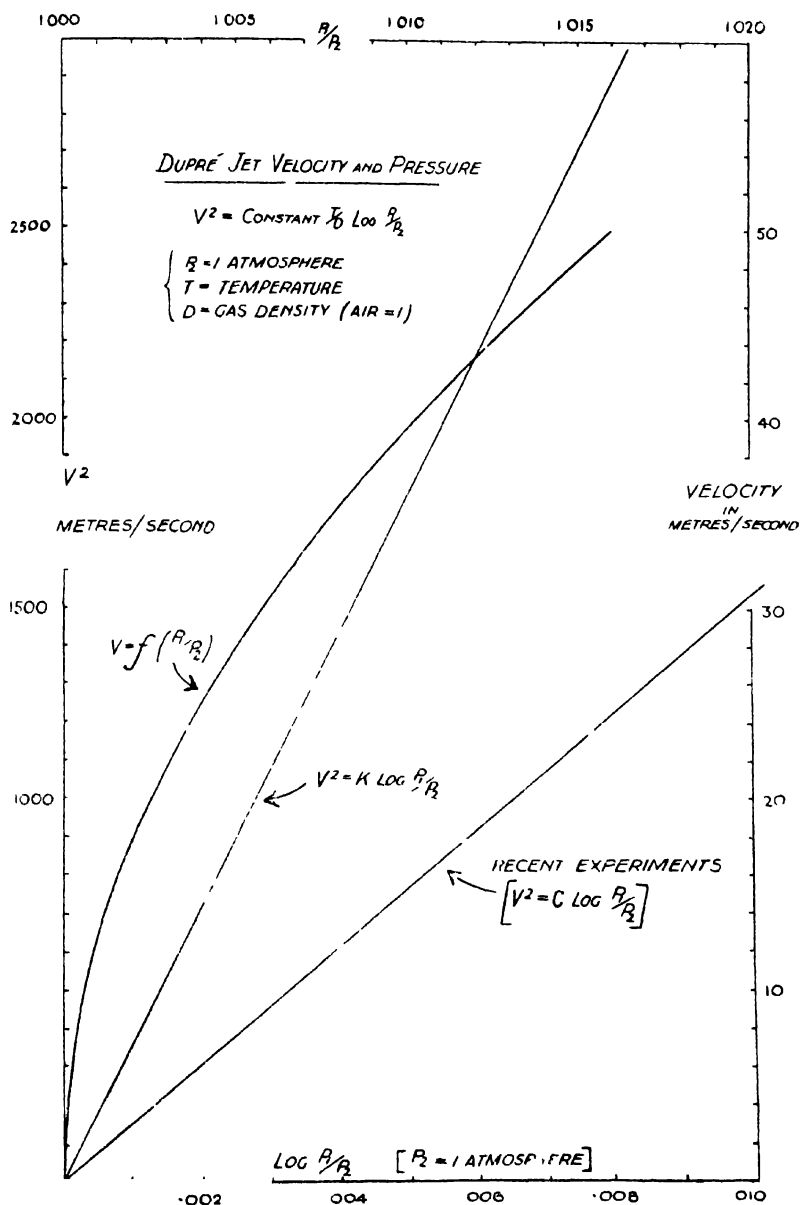


FIG. 44.

TABLE II

Platinum Jet (June 1922)

Diam of orifice = 0.024 cm

Area = 0.000452 sq. cm

Pressure cm. Water	Velocity of Jet in Met. per Sec.		
	Air	Nitrous Oxide	Hydrogen
1.0 cm	—	—	28.08
2.0 "	13.93	11.94	36.26
3.0 "	16.96	16.58	46.43
3.5 "	18.13	—	49.75
4.0 "	19.9	18.95	55.93

Platinum Foil Jets

1. Clean circle 0.987 mm diam. area 0.118 sq. mm.
Most sensitive at 74 cm. water pressure.
Volume of air then passed 143 cc. per min.
Velocity through jet 20 metres per sec.
2. Slightly distorted jet circle 0.288 mm diam. area 0.065 sq. mm.
Normal sensitiveness at 7 cm. water pressure.
Volume passed 90 cc. per min.
Velocity 23.1 metres per sec.
3. Clean circle 0.09 mm diam. area 0.00636 sq. mm.
General sensitiveness at 154 cm. water pressure.
Volume passed 28½ cc. per min.
Velocity 74.7 metres per sec.

Glass Nozzles

1. Elliptical orifice 0.63 to 0.90 mm diam. area 0.44 sq. mm.
Very sensitive, disturbed in open by even faint rustling of paper as well as by all speech.
At 1 cm. water pressure volume passing 6.67 cc. per sec.
Velocity 15 metres per sec.
2. Circular orifice 0.36 mm diam. area 0.102 sq. mm.
General sensitiveness at 2.2 cm. water pressure.
Volume passed 1.64 cc. per sec.
Velocity 16 metres per sec.
3. Elliptical orifice (slightly spiralled tube) 0.21 to 0.36 mm diam., area 0.083 sq. mm.
Wide range of sensitiveness. At 2.6 cm. water pressure volume passed 1.43 cc. per sec. and velocity 17.24 metres per sec. and at 3.5 cm. pressure volume 2.22 cc. per sec. and velocity 26.8 metres per sec.
4. Clean circular orifice, with stumpy nozzle 0.225 mm diam. area 0.04 sq. mm.
At 5 cm. water pressure volume 64 cc. per min.
Velocity 27 metres per sec.

An investigation was also begun on the effect of variations of the distance of the jet from the film upon the sensitive responses obtained; one set of observations is embodied in the curve of Fig. 45, but beyond the fact that, apart from varying the pressure, there is evidently an optimum distance and inclination for most jets,

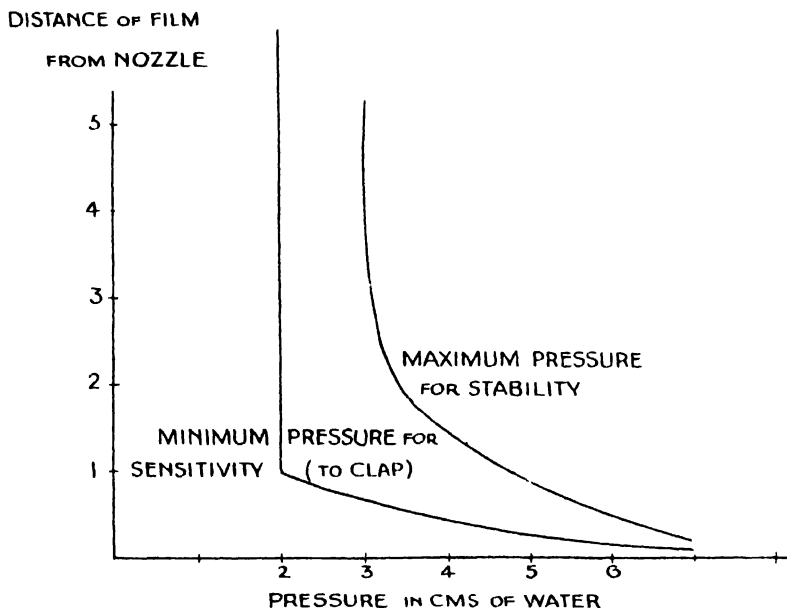


FIG. 45.

little was deduced. There were also definite instances where jets about $\frac{1}{2}$ cm. distant from the film were sensitive only to high notes, and at upwards of 2 cm. distance (nozzle to film) became sensitive only to low notes.

DETECTION OF MAGNETIC PROPERTIES OF GASES.

The film jets readily lend themselves to the study of the magnetic displacement of a stream of oxygen, and the amount of similar effects with other gases. The arrangement for this is illustrated in Fig. 46. A glass-fronted black box was fitted over the poles of an electromagnet. The soap film was on a glass tube 3 cm. in diameter, enlarged very slightly at the front end, and secured in a spring clamp

flexibly fixed on the back of the box, which had been slotted for the purpose. A similar support held a quill tube drawn out and bent up to an orifice of about $\frac{1}{2}$ mm. diameter, arranged so that a jet of gas at about 1 cm. water pressure or less impinged on the film at the end of the 3 cm. glass nozzle. Illumination was arranged as for the demonstration of Young's spectrum bands (Fig. 7), a very short focus lens having rack adjustment now being placed in the line of the beam reflected from the film. The point of impact of the jet from the small nozzle upon the film was thus clearly defined, with

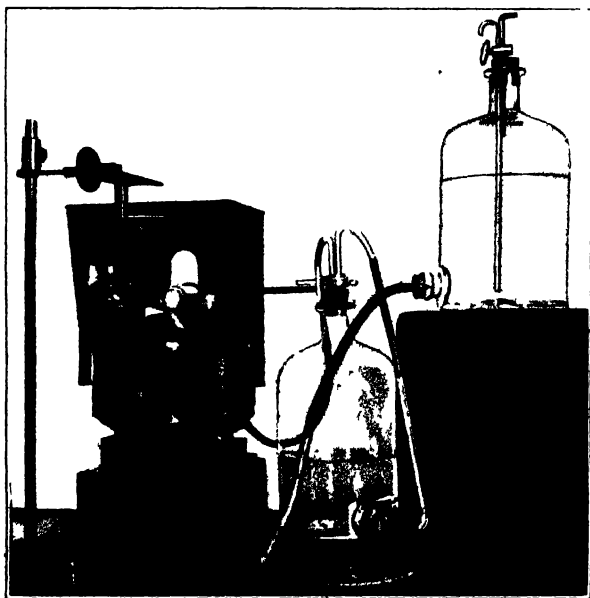


FIG. 46.

the two quiet symmetrical coloured vortices developed thereby. On establishing the magnetic field by closing the switch in the electro-magnet circuit, the impact of an oxygen jet was displaced across or even off the film, and the vortex configuration transformed. With both oxygen and helium streams the jet was drawn down towards the poles—that is, into a more intense part of the field. With air only a small positive effect was obtained, and no effect at all with nitrogen. Hydrogen gave a small negative displacement.

* Apparently an anomaly: the helium employed contained a trace of nitrogen only, so that the effect was not due to oxygen impurity.

PERFORATION OF SOAP FILMS.

For demonstrating the passage of liquid air and other drops through a horizontal film, the arrangement of Fig. 47 was used. The film ring was supported on opposite sides by vertical sliding rods with a dish of solution in the bottom of the black box, which had

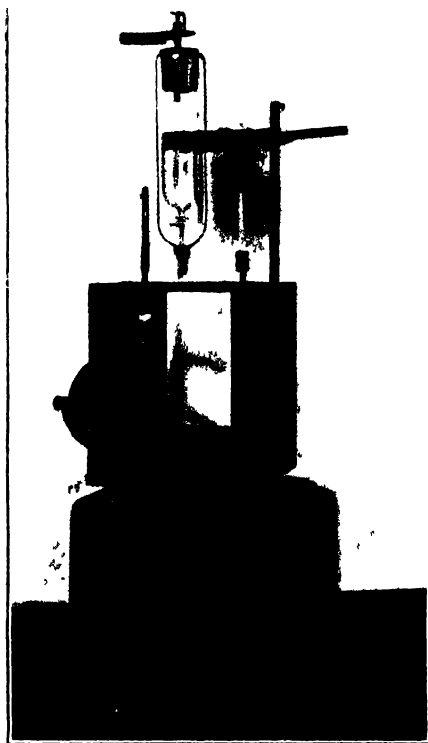


FIG. 47.

glass both front and back. The parallel arc beam was glanced down on the film and reflected through the focussing lens on the opposite side. A liquid air dropper was supported at various heights above. The passage of each drop was clearly seen on the screen by a momentary distortion of the film at the point of impact of the drops, followed by a small but rapidly projected coloured vortical movement on the

neighbouring parts of the film. A silvery film (next in thickness to the black stage) frequently survived the passage of several drops; but a black film never one. The impact of a drop near the support ring also destroyed the film. With a completely black film, on one occasion, mercury drops and lead shot, perfectly clean and dry, went through safely, and also drops of soap solution and pure water.

Not only drops of liquid air, but also of concentrated sulphuric acid, potash solution (or even small bullets of solid caustic), and mercury successfully passed through (only tried in the laboratory from a height of about 1 metre), and small lead shot, wet with soap solution or water or potash, frequently passed through, whereas if they were wet with oleic acid the film was invariably destroyed.

Drops of liquid air from the laboratory roof (a height of approximately 80 ft.) passed through a horizontal film 10 cm. in diameter. They were protected for the first 60 ft. by a 3-in. zinc pipe fixed to the wall of the yard, but even so fell at a slower rate than similar water drops. The films were formed in a cylindrical glass "gas jar," nearly a metre high and 20 cm. in diameter, kept clean by a current of pure air, the dish of solution for immersing the horizontal wire ring to form the film being in the bottom. The jar was covered while the film developed to the required thickness, and quietly uncovered while the drops fell. Under these conditions also lead shot—both dry, and wet with soap solution—and drops of soap solution itself successfully passed through the film, as also did drops of various amalgams (pushed over the edge of a glazed tile). It is certain that real contact of most of these materials would have destroyed the film, which therefore was either probably preserved by an air cushion, or else the time of contact was insufficient to start any reaction. Sulphuric acid drops were also found to bounce off an inclined film.

HORIZONTAL FILMS; MULTIPLE SYMMETRICAL VORTICES.

Vortex patterns of almost perfect symmetry and with clear definition of streaming tracks were obtained on horizontal films 19 cm. in diameter. Steatite jets were employed, but in addition to the simple single hole giving a jet normal to the film, 2, 3 and up to 10 holes were tried, accurately drilled (by Messrs. Suggs, Westminster) at equal inclinations, and equally spaced round the spherical end of the nozzle. The angle at which the jets thus impinged on the film was usually 45°, but angles of 30° and 60° were also successful. A continuous circulation of pure air was used, generally saturated by passage through glycerin of a concentration equal to that in the soap solution employed. Both inlet and outlet circuits were protected from contamination by cotton wool bulbs, the cotton wool also being wet with glycerin of the appropriate dilution. The

films were either "thrown" as previously described or were blown up into the position required by a separate tube dipping down (through a cotton wool gland tube in the stopper of the 5-litre bottle employed) into a 1-cm. layer of soap solution in the bottle. Superfluous liquid was drained away by a clean needle drawn up by a magnet into the lowest part of the film (slightly inclined for the purpose). The steatite nipple, cemented into a central glass tube adjustable through the stopper in the same way as the blowing tube, was then adjusted to a suitable height (from 1 mm. up to about 10 cm. according to the configuration required) and the air current started. A water manometer in this circuit was used for controlling the pressure, which in general was maintained fairly constant, up to 4 or 5 cm. water.

The development of the film through all stages of colour to black could be largely controlled by the pressure of the jet. Symmetrical sector-shaped vortices were produced, two to each jet. Of these one was self-enclosed—circulating out along a radius from the impact of the jet, bending round along the circumference until it met the similar stream moving to meet it from the neighbouring jet, and then bending in along a radius again towards its point of origin, where it curved into the issuing stream and again swept out along the same path. Within this outer boundary similar streams maintained their almost constant defined paths in graded colours to the centre, which sooner or later developed to the black spot. (See Fig. 48, five nozzles, and Figs. 49 and 50, four nozzles.) This black area extended continually, while the coloured streams diminished until only a fainter and fainter silvery track resulted, which finally, usually only after some hours, disappeared. The companion symmetrical vortex to the self-enclosed one just described appeared on a cursory examination to behave in the same way: but as the streaming colours became more contrasted, it was seen that, after passing out along a radius from the jet and around its portion of the circumference, it then, after bending in along a radius symmetrical to its companion vortex, did not curve again into its jet of origin, but bent in the opposite sense and was gathered into the stream from the next jet. It then continued along a similar path in the track from this second jet, and after curving in to the centre, passed on to the next jet again, thus making an endless circulation round alternate sectors of the film. There are thus two approximately equal areas of the film occupied respectively by alternate self-enclosed vortices, and by an alternate set of similarly shaped sector vortices with a continual streaming through them. The two areas thus defined are soon rendered evident by their different rates of thinning, the general appearance developing to that of two Maltese crosses of

contrasted colours occupying the whole film, each having the same number of rays as there are jets.

Figs. 51 and 52 show the later development of the vortices from a triple jet. The self-enclosed vortices become completely black before the inter-connected set, so that these last remain as a continuous coloured or silvery stream on an otherwise black film, as shown in Fig. 52. Fig. 53 shows the silvery pattern from a double jet shortly before the film becomes black, and Fig. 54 a totally different type of streaming (from a five-hole jet) when the nozzle distance is reduced to a few mm. from the film, instead of being more than 2 cm. from it as in the previous cases.

Figs. 48-55 are from photographs taken with the camera directed down at about 30° inclination to the horizontal films, which were illuminated for the purpose by a well-lighted background immediately above (all the space below the films being black). A Ross portrait lens of 8 in. focus at F. 8 or F. 11 was employed. Further details are given below :—

- Fig. 48. 5-hole nozzle: each 0.55 mm.: $1\frac{1}{2}$ cm. water pressure.
Plateau solution 4 times diluted.
Quiet colour streams in all vortices.
Backed Rapid Panchromatic plate: 75 seconds' exposure.
- Figs. 49, 50. 4-hole nozzle: 0.28 mm.: 1 cm. pressure: 10 cm. above film.
Plateau solution 6 times diluted.
Steady colour stream lines.
Same plate and exposure as Fig. 48.
- Fig. 51. 3-hole nozzle: 0.28 mm.: $1\frac{1}{2}$ cm. pressure: 8 cm. above film.
Plateau solution half strength.
Small black eyes in the colour vortices.
Same plate and exposure as Fig. 48.
- Fig. 52. 3-hole nozzle: 0.55 mm.: 1.6 cm. pressure: 3 cm. above film.
Plateau solution half strength.
Silvery streams on black film.
Wellington "Xtreme" plate: 20 seconds' exposure.
- Fig. 53. 2-hole nozzle: 0.28 mm.: 1 cm. pressure.
Plateau solution 6 times diluted.
Silvery vortices on black film.
Eclipse plate: 15 seconds' exposure.
- Fig. 54. 5-hole nozzle: 0.3 mm.: $1\frac{1}{2}$ cm. pressure: 3 mm. from film.
Half strength Plateau solution.
5 black sector vortices on silvery film with centre pentagon still coloured.
- Fig. 55. 6-hole nozzle similar to Fig. 54, but 3 cm. above film.
6 pairs of black vortices on silvery film.

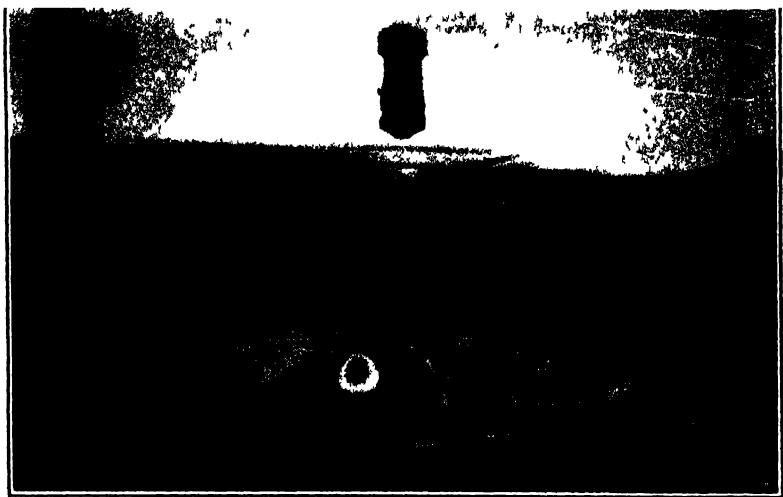


FIG. 48

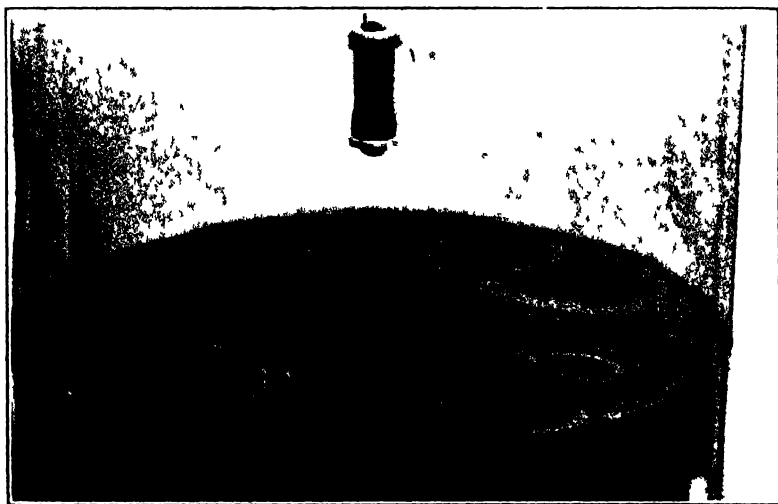


FIG. 49

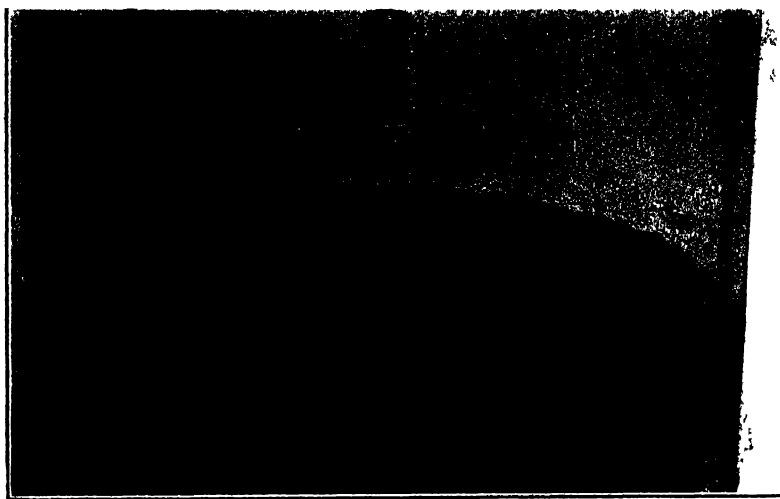


FIG. 50.



FIG. 51.

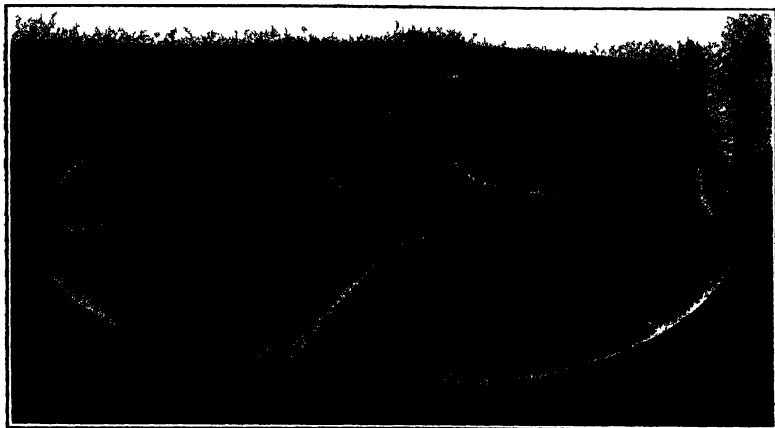


FIG 52

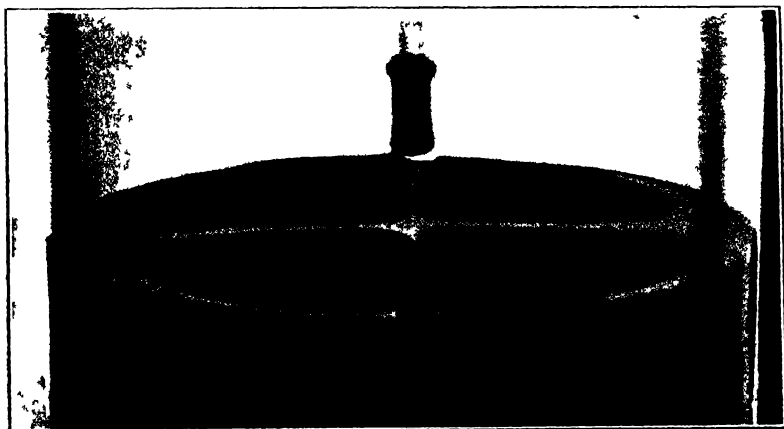


FIG 53

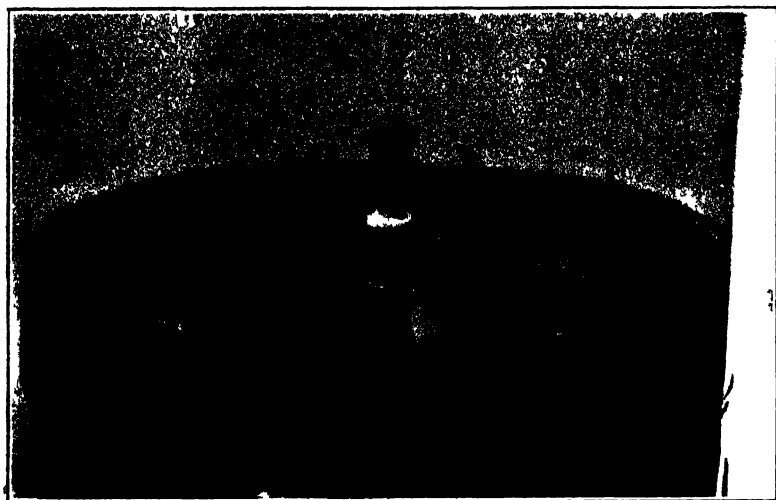


FIG 54

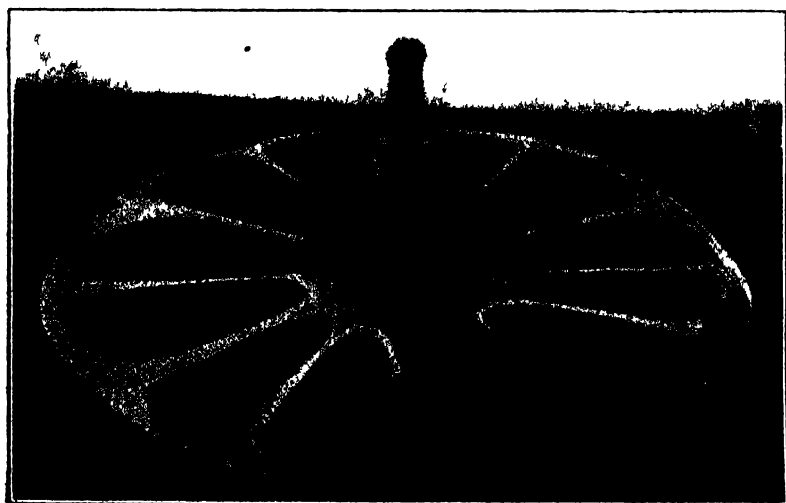


FIG 55

By carefully increasing the pressure, after the film has become completely black, more liquid can be drawn out of the Gibbs channel and the colour vortices built up in the reverse way. At suitable pressures the stream line patterns are often almost immobile, suggestive of brilliant lacquer designs: the only perceptible movement is a slight waviness in the outline of the black "eyes" in the vortices (due to slight vibration tremors, otherwise imperceptible). Under such steady conditions, if the jet be within the limits of pressure for sound sensitiveness, the path of the various streams is very strikingly demonstrated by a single sound pulse of suitable pitch and character. The simultaneous disturbances, when the sound strikes the jets, are propagated out along each separate stream, whose courses are thus marked out by the progress of the distortion wave in and out from jet to jet, or round and round in each self-enclosed vortex. The speed of the streaming is thus quite plainly demonstrated; the time for one complete circulation with a triple jet of 0.36 mm. orifice at 2.5 cm. pressure (passing 195 cc. per minute through each hole) is less than one second in and out round the 19 cm. diam. film, a total distance of approximately three diameters and half the circumference, or about 90 cm., i.e., of the order of a metre a second, as compared with about 30 metres a second air velocity through each hole.

PARALLEL FILMS; GAS VISCOSITY.

In Maxwell's original spinning-discs experiment he could detect no "viscosity" effect at a greater distance than 3 cm. from the disc in rotation. It was thought interesting to try what effects could be detected with rotating liquid discs such as the soap films provide when air jets impinge upon them.

The apparatus, of which Fig. 56 is a photograph, was devised to obtain several parallel films $14\frac{1}{2}$ cm. in diameter at certain required distances apart, for the purpose of studying how far a vortex stream on one film could be transmitted through certain gases and be reproduced on parallel films. The relative viscosities of various gases can thus be studied. The films were horizontal, and the streaming motion was obtained by a jet approximately normal to the film from a vertical nozzle below. The height of the nozzle (Fig. 57) was adjustable, and also the pressure of the air or other gas issuing therefrom. The films could be safely obtained 2 or 3 mm. apart, in number limited only by the dimensions of the container. That used was a cylindrical bulb B of $1/12$ cub. ft. capacity, familiar in the gas industry. In this on one or two occasions 13 films at 3 mm. distance were obtained. The films were formed by successive drops in a constriction in the blowing tube C above, through which a controlled current of air or other gas was passed in a manner already described.* C was a good

* *Proc. Roy. Inst.* (1918), **xxii**, p. 367.

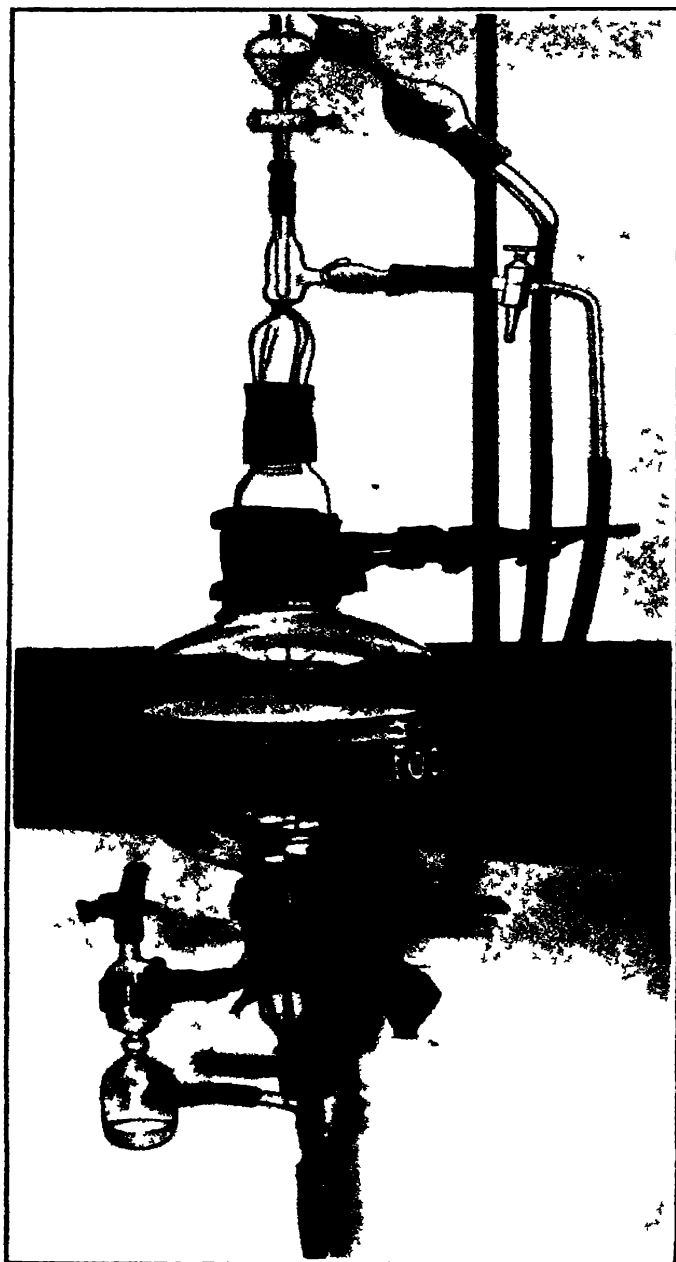


FIG 56

sliding fit in the upper part of B. clean rubber tube making an airtight joint. The soap solution was contained in the dropping funnel D, and the air current entering through E was controlled by the two-way cock G. The outlet below was a T-shaped glass fitting H, in the rubber cork closing the bulb B. The vertical part of H fitted in its lower portion round the tube I, in the top of which the nozzle A was cemented, but above this sliding fit H was widened to form an annulus round I where it opened to a horizontal outlet into the drainage bulb K. To control the positions of successive films a second outlet is necessary. This was simply a very narrow glass tube J, adjustable for height in the same way as I, and passing through the lower cork close to H.

A film having been blown down as low as required, the blowing current was interrupted by turning G. The downward motion of the film was thus stopped. The outlet tube of K was closed and J carefully raised until it just pierced the film: J was then the only outlet for the gas while the next film passed down to its required position. The space *below* the first film had then no outlet, K having been closed. The first film therefore remained stationary while the second approached as close as was desired. The blowing current having again been interrupted by turning G, J was once more raised sufficiently to pierce the second film, which in the same way then remained stationary while a third film was being brought down. After all the films had thus been obtained, they could all be lowered together by closing J, opening K,

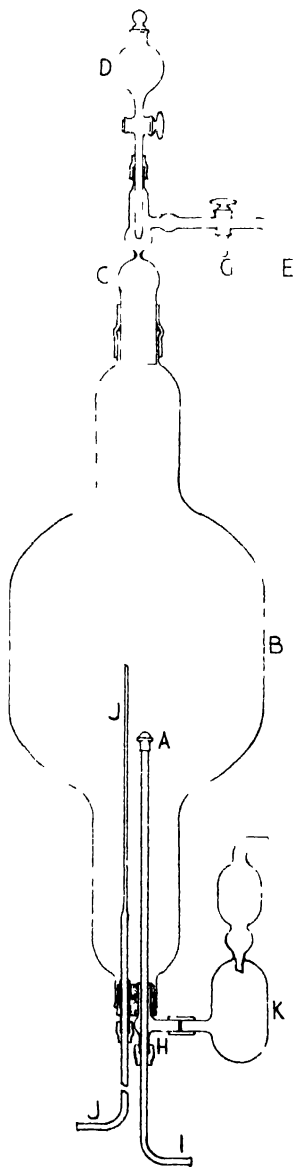


FIG. 57.

and admitting more gas through C, or they could all be raised together by using K (or I) as inlet and G as outlet. Also their relative spacing could be re-arranged by using J as inlet and either K or G as outlet (according as a downward or upward displacement was necessary), by first arranging the opening of J in the space between the two films whose distance apart was to be increased; or vice versa, with G or K (or I) as inlet and J as outlet, the distance between any two films could be decreased if, as before, the top of J opened in the space between them.

These operations naturally require care. A preliminary wetting of the entire interior is necessary. This can be done by a slow succession of single films, each succeeding one advancing further over the dry surfaces than its predecessors, until one passes entirely through the bulb and down all the length of J raised as high as possible for this purpose. J need not be more than one or two mm. in diameter, and should be as thin-walled as practicable, with its upper end cut off slanting rather than square (and of course rounded off in the flame) to facilitate its passage through the films without clinging or distortion on making or releasing contact. It is also necessary to stop the blowing while J is being passed through any film, as otherwise the film is ruptured by the rapid eddies about the narrow opening of J.

A dangerous distortion of the films occurs if superfluous liquid is allowed to accumulate round their circumference, but this is easily prevented if a single strand of cellulose (artificial silk) is secured inside the blowing nozzle C when B and C are being assembled. A few preliminary films wrap the cellulose close to the contour of B from top to bottom, where it remains and very effectively drains away the liquid accumulating round the ring contact of the films with the glass.

Details of Experiments.

AIR.

6 films spaced 0.75 to 0.8 cm. apart. Plateau solution.

Single steatite nozzle, 0.3 mm. hole.

Jet normally from below at 3 cm. distance below lowest films.

Superfluous liquid removed (cellulose thread), but films all still coloured.

Fourth film up was just disturbed (*i.e.* at distance of 2.3 cm.).

Steady double eddy in lowest; rotation period $1\frac{1}{2}$ sec. ($\frac{1}{2}$ mm. dent in lowest film caused by impact of jet).

Similar double eddy in next film, but at half the rate of rotation.

Slow drift in 3rd film and small fluctuating movements in 4th.

5th and 6th unaffected.

Moving films all black in $2\frac{1}{2}$ hours: eddies then deep black.

HYDROGEN.

6 films in hydrogen all 1 cm. apart.

Same single vertical nozzle less than 4 cm. below lowest film. Jet pressure 1.5 cm. of water

Steady double symmetrical vortices of diminishing velocity in 3 lowest.

Slow movements in 4th up, 3 cm. distance.

No streaming in upper two. All coloured, but drained.

In 5 min. black centres, 2 to 3 cm. wide, in the double vortices in lowest. Rotation less than 1 sec.

7 films in hydrogen 0.73 to 0.96 cm. apart as follows (well drained as described).

Starting from the lowest the separating distances were:—0.74, 0.78, 0.73, 0.83, 0.86, 0.82 cm

Same nozzle 5 cm. below lowest film. Pressure 2.0 cm. of water.

Steady slow swirl in the 5th film, i.e. 3.22 cm above the lowest.

When the lowest film went, the motion was seen in the 6th film, 3.10 cm. above the lowest remaining film.

After 10 min. the films had thinned to partial blackness, and a definite, slow, but continuous circular drift was proceeding in the top film, 4.02 cm above the lowest

After 35 min. the appearance was as follows.—Lowest film—steady symmetrical eddy in an amber-coloured film: black ellipses 2 to 3 cm. in diameter at the "eyes" of the vortices, next two films all black. 4th film had a trace of colour, two uppermost 15 per cent. black and 85 per cent. coloured vortices on silvery background. A very slow but continuous drift in the top film: all the others in increasingly rapid motion down to the lowest.

After 65 min. the lowest film had only a trace of colour. The next three were practically all black (motion seen by deeper black vortices). Upper two still had 80 per cent. silvery with coloured vortex "eyes" in slow, steady motion.

The motion is thus transmitted through 4.02 cm. of hydrogen.

When this was repeated with fewer intermediate films between the upper and the lower, the effect was transmitted only through a space of 3.2 cm., as compared with 4 cm. when 5 films were used more closely spaced.

NITROUS OXIDE.

5 films, 0·7 to 0·8 cm. spacing.

Nozzles $3\frac{1}{2}$ cm. below lowest. Jet pressure 3·0 cm.

Motion transmitted only through 1·6 cm.

Good rapid double vortex in lowest; 3rd film up showed only a flickering disturbance.

The motion rapidly aggregates the colour into large discs rotating on the black. In $1\frac{1}{2}$ hour the films were all clean black, except for a mass of misty silvery discs rotating in the lowest film.

Repeated with 7 films spaced as follows and allowed to thin to silvery and black before starting this jet. Spacing from highest to lowest:—0·39, 0·47, 0·41, 0·40, 0·50, 0·54 cm.

Nozzle approximately 4 cm. below lowest. Pressure 2·8 cm. of water.

No disturbance could be seen at a distance of 1·85 cm. (5th film up), and only indefinitely at 1·44 cm. (4th film up).

Friday, May 4, 1923.

SIR JAMES CRICHTON-BROWNE, M.D. LL.D. F.R.S., Treasurer
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The Origins of the Conception of Isotopes.

ONE of the most important consequences of the study of the chemistry of the products of radioactive change has been the discovery of isotopes and the interpretation in consequence of the Periodic Law in terms of modern views of atomic structure. It is one of the few fields in the vast borderland between physics and chemistry, overrun of recent years by an advancing swarm of mathematicians and physicists, armed with all sorts of new-fangled weapons, in which the invaders have found the chemist already in possession. The broad highways they have hewn thereto are already dusty with the tread of pilgrims, and are being watered by the tears of candidates for "Honours." But the somewhat intricate bye-ways through which the chemist first found his way into this virgin territory, and the views on the road before it was in sight, may still preserve something of their pristine interest.

The word *isotope* signifies "the same place," in allusion to isotopes occupying the same place in the Periodic Table. Before this word of theoretical meaning was coined, isotopes were experimentally well known as elements non-separable by chemical methods and completely identical in their whole chemical character. The analysis of the constituents of matter, to which we were born and brought up to regard as the most searching and fundamental, is an analysis by means of its chemical properties. Although, later, a new and even more powerful method, spectroscopic analysis, was developed, it merely dotted the *i*'s and crossed the *t*'s of chemical analysis, filled in a few vacant places in the Periodic Law, and handed over the newcomers to the chemist to classify along with the rest of the eighty or so "foundation stones" of which he supposed the material universe to be built up. Then, with the close of last century, another new method, radioactive analysis, was developed, which is applicable of course only to the radio-elements—that is, to the elements uranium and thorium and the thirty-four, as we now

know, successive unstable products of their spontaneous disintegration. Each of these possesses a definite radioactive character; it is produced from one and changes into another element, and, in both changes, rays characteristic of the two substances are expelled, which are as fine a hall-mark of their identity as any of the "tests" of chemical analysis. But radioactive character, unlike spectroscopic character, is completely independent of chemical character. The latter might be called "existence properties," whereas the radioactive character is that attending the explosion of the atom which terminates the existence of the element as such. It provided the necessary independent method of analysis capable for the first time of distinguishing between elements identical chemically and occupying the same place in the Periodic Table—i.e. between isotopes.

THE EARLIER CHAPTER OF RADIO-CHEMISTRY.

Not a hint of this, however, was afforded by the earlier chapter of radio-chemistry. On the contrary no development could appear more normal. Just as rubidium, thallium, etc., were detected by the spectroscope before anything of their chemistry was known, so radium was detected in pitchblende by its radioactivity in concentration thousands of times less than is necessary to show a single line of its spectrum. But with more concentrated preparations a new spectrum *was* discovered, and then a new element, which was found to possess a chemical character entirely new and sufficing for its separation in the pure state from all other elements. As in the case of the elements discovered by the spectroscope, radium was found to occupy a place, hitherto vacant, in the Periodic Table. But as it happened radium is exceptional in this. Its chemical character was quite normal, and indeed could have been largely predicted beforehand for the missing element occupying this place. The development of the subject showed it to be but one of some thirty-four radio-elements formed from uranium and thorium. But there are not thirty-four vacant places in the Periodic Table to accommodate them.

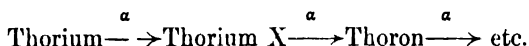
META-ELEMENTS.

So far as I am aware, there is no anticipation, prior to the systematic study of the chemistry of the radio-elements, of the idea that there may exist different elements with absolutely identical chemical character. Sir William Crookes, it is true, once thought, though the idea has not survived more extended examination, that the properties of the elements, as we know them, might be a mean value, and that the individual atoms composing the element might differ in weight and chemical character continuously on either side of this mean. If so, more refined methods might serve to resolve the element into a collection of what he termed "Meta-Elements,"

possessing the main character of the original, but differing from one another to a slight extent. Misled by the phosphorescence spectra, which are now known to be characteristic of mixtures rather than chemically homogeneous substances, he thought at one time that he had been successful in so resolving yttrium. But the present idea that elements may exist, absolutely the same in chemical nature and yet absolutely different in other properties, such as radioactivity and atomic weight, is totally distinct from this.

THE EXPERIMENTAL METHOD THAT FIRST REVEALED ISOTOPES.

I venture to think that no more elegant extension of our methods of gaining new knowledge has ever been obtained than that which, in due course, was to reveal the existence of isotopes. The original observations, upon which the theory of atomic disintegration was first founded, were that thorium is continuously producing a new radioactive substance, thorium X, separable from it by precipitation with ammonia, but not with other precipitants, and, after separation, continuously re-forming again. The thorium X was short-lived, and changed again into a gas, the thorium emanation, for which the name thoron has recently been proposed, which was even shorter-lived and changed again to a solid, the "excited activity," now known as the active deposit, which again went through further changes. The rays resulted from these successive changes, α -rays in the first, and α -, β - and γ -rays in the last changes. Below is the first part of the thorium disintegration series as it appeared to Sir Ernest Rutherford and myself in 1903 :—



In 1905 Sir William Ramsay and O. Hahn were engaged in extracting radium from thorianite, a new Ceylon mineral containing both uranium and thorium in important quantities. The radium was separated with the barium, and the chlorides fractionated in the usual way. They found a new radio-element to be present, and to be separated from the radium with the barium. It proved to be the direct parent of thorium X, and intermediate in the series between the latter and thorium, and they called it radiothorium. In spite of this easy and apparently straightforward separation, the experience of a number of chemists showed that something remained to be explained, for it was found to be difficult to the verge of impossibility to separate radiothorium from thorium. Ramsay and Hahn had in fact "separated" isotopes in 1905, for radiothorium and thorium are isotopes. Yet further work has shown the two to be so alike that no separation by chemical means is possible :

Then in 1907, along with the radium which had been separated from thorianite, Hahn discovered another new radio-element, meso-

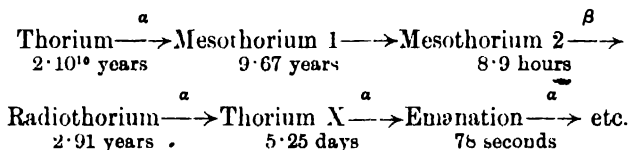
thorium, the direct parent of radiothorium and intermediate between it and thorium. In the next year he showed that mesothorium consists of two successive products—the first, the direct product of thorium, mesothorium 1, being practically rayless and generating a short-lived product, mesothorium 2, giving powerful β - and γ -rays.

This resolved the mystery, and one cannot do better than to quote the words of McCoy and Ross (J. Amer. Chem. Soc., 1907, 29, 1709):

“Our experiments strongly indicate that radiothorium is entirely inseparable from thorium by chemical processes. . . . The isolation of radiothorium from thorianite and from pure thorium nitrate . . . may have been accomplished by the separation of mesothorium, which in time changed spontaneously into radiothorium.”

Thus the radiothorium separated from the mineral thorianite by Ramsay and Hahn was not the radiothorium *in the mineral*, but that subsequently produced from the easily separated mesothorium, after it had been removed from the thorium. If they had fractionated the radium-mesothorium-barium mixture at once they would not have discovered radiothorium. The lapse of time after the separation of the mesothorium is essential. Nowadays many non-separable radio-elements, are, like radiothorium, “grown” from their separable parents. Thus radium D, an isotope of lead, is grown from the radium emanation (radon), although it cannot be separated from the mineral, which always contains lead in quantity.

The first part of the thorium series now runs* :—



In this series thorium and radiothorium and mesothorium and thorium X are two pairs of isotopes. If we represent the successive products by balls of different colours to indicate their chemical character, isotopes being of the same colour, chemical analysis will sort the balls into their different colours, and the lapse of time will cause some of the colours to change. The ball representing mesothorium will in time turn into that representing radiothorium, so that the latter, before indistinguishable from thorium, becomes known as a separate individual.

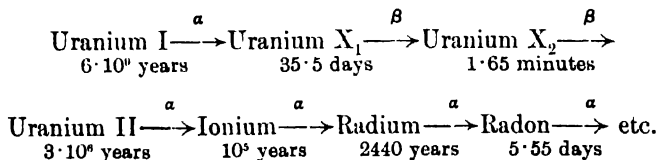
THE ISOTOPES OF URANIUM.

It will be noted that the method of separating isotopes depends upon their being alternate rather than successive in the series. If

* The periods shown in the second line are the periods of average life of the successive products. These are 1.443 times the period required for one-half of the element to change.

radiothorium had been the direct product of thorium, the two would never have been separated to this day. The changes of chemical character are, as we shall later see, intimately connected with the electric charges on the α - and β -particles expelled. For successive products to have the same character no rays, or at least no charged particles, must be expelled. It is always as well—and no subject illustrates the point better than that of isotopes—to reflect not only upon what our methods are able to reveal, but also upon what they cannot reveal.

At first it seemed as if uranium itself was a case of successive isotopes. Boltwood in 1908 proved from his study of the relative activities of the successive products giving α -rays in minerals, that whereas all of them, except uranium, gave off only one α -particle per atom disintegrating, uranium gave off two. By direct observation with the scintillation method it was proved that the two α -particles from uranium are *not* simultaneously expelled, and later it was shown that they possess different velocities. If the slower comes from uranium itself (uranium I), the period of which is known to be $6 \cdot 10^9$ years, the swifter must come from the isotope (uranium II), and its period must be some three million years. This is an example of isotopes being revealed by difference of radioactive nature simply, though no other evidence of their separate existences is available. Owing to the long periods of the α -ray giving members of the early part of the uranium series, it has been much more difficult to unravel than the thorium series. As a result of researches too numerous to detail, it has been concluded that the main series is almost entirely analogous to the thorium series, and runs:—



Though two short-lived products probably intervene between the two uraniums, analogous to the two mesothoriums between thorium and radiothorium, the relation of their period to that of their product, uranium II, is so hopelessly unfavourable that there is no hope of ever being able to put the separate existence of uranium II into evidence in the same way as was done for radiothorium. For all *practical* purposes the two uraniums are as non-separable by this method as if they were actually successive products. I spent many years, before this part of the series was at all well known, looking for the product of uranium X, and separated this constituent from 50 kilograms of uranium nitrate repeatedly in the attempt. I was looking for a growth of α -rays concomitantly with the decay of the

β -rays of the uranium X. If the product had been ionium, as at first thought ($U I \xrightarrow{\alpha} U II \xrightarrow{\alpha} U X \xrightarrow{\beta} Io \xrightarrow{\alpha}$), it should have been just possible to detect it. But since it is the thirty times longer-lived uranium II, the attempt is hopeless, especially as uranium X and ionium are isotopes, and therefore the uranium X separated must always possess a certain initial α -activity due to ionium.

THE ABSOLUTE CHEMICAL IDENTITY OF ISOTOPES AND ITS IMPLICATIONS.

The years 1908-1910 were productive of many prolonged and serious efforts to separate isotopes by chemical means. In 1908 Boltwood discovered ionium, and showed that it resembled thorium. Keetman, who with Marckwald discovered ionium independently, tried twelve good methods, all known to be effective, in the purification of thorium in the attempt to separate the ionium from thorium, completely without success. Auer von Welsbach, on a technical scale, separated the ionium and thorium from 30 tons of pitchblende, and tried fresh methods in the hope of separating them, but failed. It was with this preparation that Exner and Haschek tried without success to find the ionium spectrum, and Russell and Rossi confirmed their result, that the spectrum was that of pure thorium. When later I had determined beyond doubt, from measurements of the rate of growth of radium from uranium, that the period of ionium was 100,000 years, and that Welsbach's preparation must have been approximately 30 per cent ionium and 70 per cent thorium by weight, it followed that the spectra of isotopes must, like their chemical character, also be identical. The difference, if any exists, is almost beyond the limit of detection by the most powerful methods.

Similarly, the chemical identity of radium D and lead was established as a consequence of very prolonged and refined chemical examination. Paneth and Hevesy established upon this their well-known method of using radioactive isotopes as indicators for elements in too small quantity to be dealt with except by such methods. On the principle that wherever the radioactive element is there will its inactive isotope be also, provided that they have once been properly mixed, many difficult or uncertain chemical analyses may be converted into simple radioactive ones.

In 1909 Strömholm and Svedberg made what was probably the first attempt to fit a part of the disintegration series into the Periodic Table, and although the effort in itself was in an important respect erroneous, in their paper is to be found the first anticipation that the chemical non-separability found for certain pairs and groups of radio-elements may also apply to the non-radioactive elements. Remarking on the fact that there are three parallel and independent

radioactive series, they suppose this to proceed down through the Periodic Table, "but that always the three elements of the different genetic series, which thus together occupy one place in the periodic system, are so alike that they always occur together, and also have not been able to be appreciably separated in the laboratory." They point out also this idea would explain the exceptions to the periodic system "if the elements of the scheme were mixtures of several homogeneous elements of similar but not completely identical atomic weight."

In the next year I arrived independently, and without in the least postulating any continuance of the genetic series beyond the radio-elements, at a similar view. Marckwald and I found independently that mesothorium I was chemically similar to radium, a fact undoubtedly known to Hahn and those engaged in the technical extraction of mesothorium, but kept secret. It was known from some work of Boltwood that precipitating barium sulphate in a solution containing mesothorium removes it, but it was thought that the action of the barium sulphate was similar to that in removing uranium X, for which it had long been used namely, a simple adsorption. I was surprised to find it absolutely different. The removal of the barium from the mesothorium, as from radium, could only be accomplished by the fractional crystallisation of the chlorides. In this fractionation the radium and mesothorium remained together and behaved as a single element. Within the limit of error of the most careful radioactive measurements, there was no change in the relative proportion of the two elements at the end of the process, from that in which they exist in the original mineral. Chemistry has many cases of elements similar in chemical character, but nothing approaching this. For we know, beforehand, that we are dealing with a mixture of two substances, and can estimate accurately the proportion of each individual. Yet to all chemical operations they behave as a single substance. The differences of atomic weight are considerable, two units in the cases of mesothorium and radium, and of ionium and thorium, and four units in that of radiothorium and thorium. It was certain that if isotopes existed in the case of the ordinary chemical elements, the absence of a second radioactive nature independent of the chemical nature would make it impossible for them to have been recognised. Hence the implication followed that any supposed element may be a mixture of several chemical identities of different atomic weight, and any atomic weight might be merely a mean number (*Ann. Reports, Chem. Soc.*, 1910, 286). There is an element of tragedy in this. The life time labours of the chemists who, since the time of Stas, have devoted themselves to the exact determination of atomic weight, appear to have as little theoretical interest now, as if you sought to determine the average weight of a collection of beer bottles, all exactly alike, but not all quite full.

THE RADIO-ELEMENTS AND THE PERIODIC LAW.

The years from 1911-1913 were crowded with important advances, and to do the exact history justice would take an undue share of the available time. In 1911 the chemistry of most of the α -ray giving members were sufficiently known for it to be seen that the expulsion of the α -particle caused the element expelling it to move from the place it occupied in the Periodic Table to the next place but one to it in the direction of diminishing mass.

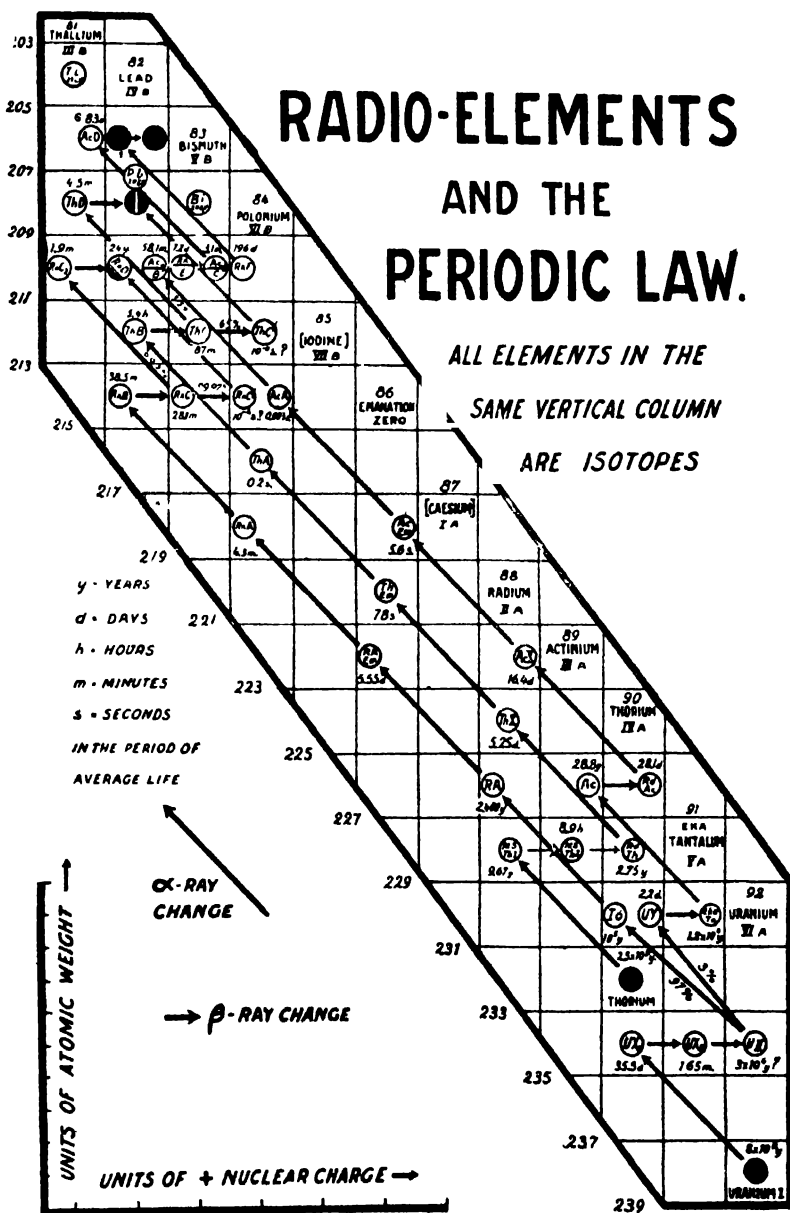
At this time the chemistry of the post-emanation members had scarcely been studied, though von Lerch, from electrochemical researches, had put forward the rule that the successive products are each electrochemically "nobler" than the last, a rule which describes well enough the electrochemical behaviour of the first three—the A to C members, as they are called. Then as a result of the experiments of Schrader and Russell, it was found that their volatility was much affected by chemical treatment and by the atmosphere in which they were volatilised. Thus, in hydrogen, radium C volatilises at as low a temperature as 360 °C., though, in air, a temperature of 1200 °C. is necessary. This clearly indicated the possibility that even these excessively ephemeral elements have a definite chemical character. Hevesy showed, by electrochemical methods, that the three B-members are identical in properties among themselves, and also the three C-members.

But the work, which, more than anything else, served to reveal as in a flash the simple and sweeping generalisation which covers the evolution of the radioactive elements was that of A. Fleck in my laboratory in Glasgow. He studied the chemistry of the various members, still uncharacterised, from the definite point of view of ascertaining to which element each most closely approximated in chemical character, and then whether it was separable from that element or not. In addition to confirming more rigorously many conclusions already reached, he proved that mesothorium 2 was non-separable from actinium, the three B-members from lead, like radium D, and the three C-members and radium E from bismuth.

Hevesy and Russell—the first with regard to the valency of the radio-elements and the second with regard to the positions they occupy in the Periodic Table—published early in 1913 statements of the full law underlying radioactive evolution, but only in part correct. Within a month K. Fajans in Karlsruhe published the scheme correct and complete, including the complicated branchings that occur at the C-members. In a paper, amplifying and amending Russell's scheme, I arrived independently at the same place as Fajans. Each α -ray expelled causes a shift of two places in the Periodic Table in the direction of diminishing mass, and each β -ray a shift of one place in the opposite direction. In its present form the scheme is

RADIO-ELEMENTS AND THE PERIODIC LAW.

ALL ELEMENTS IN THE
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shown in the figure. The chief uncertainty remaining is whether the actinium branch starts from uranium II, as shown in the figure for convenience, or from uranium I, or even from a third independent isotope of uranium. So that the atomic weights shown for the actinium series are purely provisional.

By the consistent application of the two rules mentioned the members found to be non-separable from one another fall in the same place in the Periodic Table. The chemical character has nothing to do with the radioactivity, nor with the series to which the element belongs, nor with its atomic weight. It depends upon a number, now called the atomic number, shown at the top of the place in the figure.

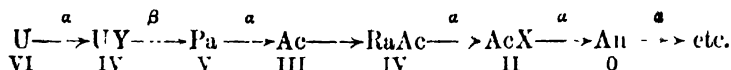
Before passing on to this, the chief practical consequences of the generalisation may be briefly enumerated.

(1) Of the members still uncharacterised, the A and C' members must be the isotopes of polonium (radium F), and radium C₂ (now called radium C'''), actinium D and thorium D must be isotopes of thallium. Fleck at once verified these predictions as regards radium A, actinium D and thorium D.

(2) Uranium X, like mesothorium, must consist of two successive β -ray giving products, intermediate between the two uranums. Fajans and Gohring at once succeeded in separating from "uranium X" a very short-lived product, uranium X₂, giving the more penetrating of the two types of β -ray expelled, the uranium X₁ giving the less penetrating β -rays.

(3) The parent of actinium in the IIIrd family must be an isotope of radium, if actinium is formed in a β -ray change a conclusion I at once experimentally disproved or it must be an isotope of uranium X₂, in the Vth family, if actinium is formed in an α -ray change. This was proved by Cranston and myself, and the name "eka-tantalum" given to the new element, and by Hahn and Meitner, who named it protoactinium. It is linked to uranium through uranium Y, a branch member discovered by Antonoff in 1911, and suspected to be in the actinium series.

Protoactinium, to give it Hahn and Meitner's name, has been shown by them to give α -rays, and to be chemically so like tantalum that hitherto it has not been separated from it. Its period is about 17,000 years, and from this it may be calculated that there is about one-fifth as much of it by weight in minerals as there is of radium. This may be sufficient to enable it to be isolated and for its spectrum, atomic weight and chemical character to be ascertained. The branch series runs:—



in which the figures in the second line refer to the family in the Periodic Table to which the element belongs.

(4) All the ultimate products in all branches are isotopes of lead. The atomic weight of the two products of thorium are both 208, and of the major branch of uranium 206. As is well known this had only to be tested to be proved correct. The atomic weight of the lead from the purest thorium minerals is as high as 207.9, and of that from the purest uranium minerals 206. The spectra of these isotopes, but for the possible infinitesimal difference already alluded to, are identical. But the densities are proportional to their atomic weights. This was a very simple prediction I made, before testing it, from the theoretical views about to be dealt with.

THE THEORETICAL INTERPRETATION OF ISOTOPES.

The results on the theoretical side were no less definite and important, and isotopes found a ready explanation on the nuclear theory of atomic structure put forward in a tentative form by Rutherford in 1911. This theory accounted for the large angles through which occasional α -particles were deflected in their passage through atoms, by the existence of a very minute highly charged nucleus at the centre of the atom, the rest of the atom being occupied by separate charges of opposite sign equal in number to the nuclear charge. For such an atom scattering should be proportional to the square of the nuclear charge. Experiment showed that scattering was approximately proportional to the square of the atomic weight. So that it looked as if, as in the α -particle itself, there existed one unit of nuclear charge to each two units of atomic weight. This would make the nuclear charge of uranium, of atomic weight about 246, $120 +$.

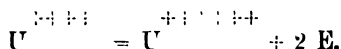
Since the α -particle carries two positive charges and the β -particle one negative, the obvious inference from the figure is that the successive places in the Periodic Table correspond with unit difference in the intra-atomic charge. This view, and also that each unit of charge corresponded to two units of mass, had been suggested independently by van der Broek in 1911. At first he tried to stretch the Periodic Table to make it accommodate 120 places. But, in 1913, he pointed out that the experimental results for scattering were completely in accord with his own view (that the number of the place is the same as the intra-atomic charge). *on the existing Periodic Table*, which accommodates only some 90 elements. It would not be inconsistent with his other view (that the nuclei of the heavy elements are made up of helium nuclei) if there were electrons in the nucleus as well as in the outside shell. Thus uranium in the 90th place would have to have, in addition to the 60 helium nuclei in its nucleus to account for its weight, 30 electrons, to account for its charge of $90 +$.

The existence of electrons as well as positive charges in the atomic nucleus was also postulated by Bohr to explain the emission

of β -rays, for on his theory the electrons in the external shell form a stable configuration and could only be dislodged by the expenditure of work.

The Periodic Law generalisation practically settled this question. β -ray changes are no less transmutational than α -ray changes, and are sharply to be distinguished from the numerous processes, such as friction, chemical change, action of ultra-violet light and incandescence, during which electrons are detached from atoms. The effect on the chemical character produced by the expulsion of one α -particle is exactly undone by the expulsion of two β -particles, and the product becomes isotopic with the original parent. This means that both α - and β -particles must be expelled from the nucleus, and that isotopes are elements the atoms of which have the same *net* nuclear charge – i.e. the same excess number of positive over negative charges in the nucleus, but different numbers of positives and negatives reckoned separately. For such systems the electronic shell would be identical, and so the identity of the chemical and spectroscopic character is explained. Also the atomic volume is the same – that is, the density must be proportional to the atomic weight.

We were able to get an interesting confirmation of this view. In the change of uranium X_1 to uranium II two electrons are lost as β -rays. In the oxidation of a uranous salt to a uranic or uranyl salt two electrons are also lost.



If these come from the same region of the atom as the β -particles, then uranous salts, so long as their valency does not change, should be like uranium X_1 , chemically non-separable from thorium. Fleck, trying this, found great similarity in chemical properties between uranous salts and thorium, but not identity. He was able to separate them by chemical methods without changing the valency of the uranous salt.

The great merit of the nuclear atom from the chemist's point of view was that it afforded for the first time a clear picture of the difference between a chemical and a transmutational (or radioactive) change. The latter occur in the nucleus and are irreversible. The external shell accommodates itself instantly to the change of the nucleus. But any change suffered by the external shell (chemical change) has no effect on the nucleus, which always acts so as to make the external shell conform to one most stable configuration.

The atom is an *imperium in imperio*, and like most such systems is very conservative and resistant to change. The electrons in the shell, that govern almost all the atomic properties, except mass and radioactivity, are in turn but the bureaucratic instruments of the real government, which is the intensely charged central nucleus. The transmutation of atoms, as of social systems, is alike impossible

because the apparent government is not the real government. Rutherford's experiments, on the bombardment of atoms by α -particles, show that only about one out of a hundred thousand of the latter in passing through hydrogen ever hit a hydrogen nucleus, and the proportion of hits to misses is something like one in one thousand millions. In politics, contrasting the number of missiles hurled with the results achieved, the shooting seems even worse. It is only when the atomic or social systems break up or break down that we learn even of the existence of their real internal constitution.

[F. S.]

Friday, May 11, 1923.

SIR ARTHUR KEITH, M.D. LL.D. F.R.S., Secretary and
Vice-President, in the Chair.

WILLIAM A. BONE, D.Sc. Ph.D. F.R.S.,
Professor of Chemical Technology at the Imperial College
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Gaseous Combustion at High Pressures: New Experiments.

INTRODUCTION.

IN the course of the researches upon gaseous combustion which for many years past have been carried out in my laboratories, it became necessary to study the subject under much higher pressures than those heretofore employed. And as this aspect of the work has recently assumed greater importance from the standpoint of the mechanism of combustion than was at one time foreseen, I have chosen it as the theme of my discourse to-night.

The scientific investigation of Flame, which originated rather more than a century ago with Sir Humphry Davy's researches in this Institution, has always had a fascination for chemists, and as yet there seems no end to it. For we are still far from understanding completely even the simplest known cases of gaseous combustion; and it is upon some of these that our high pressure researches have thrown new light.

APPARATUS AND METHOD.

Before, however, proceeding to explain what these new observations have been, it will be necessary for me to say something about the apparatus and methods which have been designed and employed for such work. For they must obviously differ from those ordinarily used for experiments at atmospheric pressure where the conditions are much less severe.

In the first place, it is necessary to carry out the experiments in specially designed vessels of forged steel capable of withstanding the sudden development of very high explosion pressures. Thus, for example, the initial pressures at which the combustible mixtures are fired in our experiments range up to 50 and, in extreme cases, even

up to 100 atmospheres. And the resulting pressures, which are developed in a small fraction of a second, may be anything up to ten times as great. Hence our explosion vessels and their accessory valves and fittings must be capable of withstanding pressures up to 1000 atmospheres suddenly developed; and the method of measuring and recording pressures must be capable of following accurately, and with the least possible lag, a rise of pressure of from (say) 50 to 500 atmospheres occurring within $\frac{1}{200}$ th of a second.

The bomb (Fig. 1) which has been employed in our recent experiments^{*} was machined out of a solid forging of open-hearth steel. Outwardly it is cylindrical in outline (10·25 inches long by 8 inches diameter), and out of its central part had been cut a spherical cavity A about 3 inches in diameter (capacity *circa* 240 cc.). It is

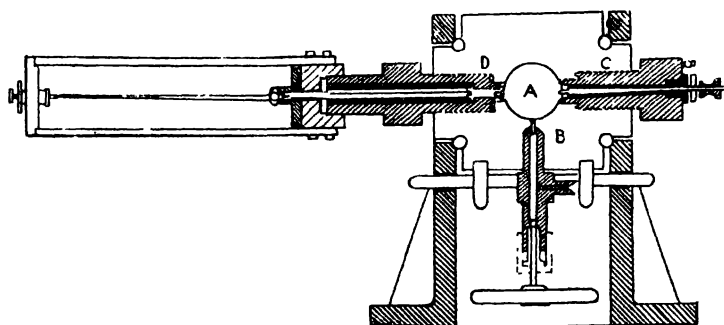


FIG. 1.

mounted on a cast-iron stand by means of ball bearings which permit of a rapid rotation of the bomb on its axis in order to ensure an effective mixing of its gaseous contents before an explosion. As used in an experiment the bomb is fitted with an admission valve B, an ignition plug C, and a Petavel manometer D. The mixtures are ignited by means of a platinum wire heated to incandescence by a direct electric current from a battery of secondary cells (12 volts); and the ignition wire is situated near the wall of the explosion cavity immediately opposite the head of the Petavel manometer.[†]

^{*} I must here acknowledge the devoted assistance in these researches of the late W. A. Haward, M.Sc., who lost his life in a deplorable accident whilst engaged upon them, and afterwards of Messrs. D. M. Newitt, B.Sc. D.I.C., and D. T. A. Townend, B.Sc. D.I.C., who are still collaborating with me.

[†] A full description of the bomb and principal accessory appliances employed in the research will be found in Phil. Trans. Roy. Soc., A. 215 (1915), pp. 275-363.

An essential part of the installation is the recording manometer of the form designed by Prof. (now Sir J. E.) Petavel in 1905* (Fig. 2), which is a most efficient appliance for high pressure work.

Perhaps the action of the gauge will be understood when I say that, together with its optical accessories, it measures, and by a magnifying device records, the outward bulge on the walls of the explosion cavity caused by the pressure developed when the combustible mixture is fired therein. Now the time period θ of a vibrating system is related to W , the weight of its moving parts, and to the force A required to produce unit deflection, as follows :--

$$\theta = 2\pi \sqrt{\frac{W}{A}}$$

In the Petavel gauge the time θ is made as short as possible consistent with the required strength (W) to withstand the sudden development of extremely high pressures, by making A , the controlling force brought into play per unit length of motion, as large as possible ;

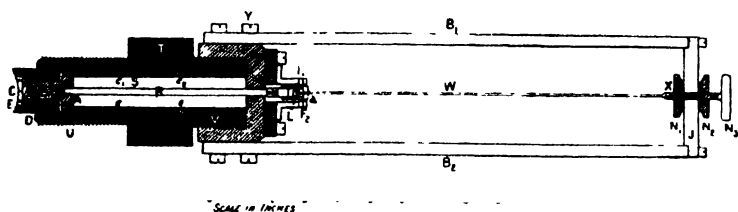


FIG. 2.

or, in other words, by using the stiffest spring possible. By such means the time lag in registering the pressure is reduced to a minimum, which is always a most important consideration in experiments of this kind.

The spring of the gauge is tubular in shape : the actual motion produced in it by the explosion is exceedingly small, and for recording purposes it is highly magnified first of all (*a*) by a special lever device in the gauge itself, and then (*b*) by an outside optical arrangement (Fig. 3) which focuses a point source of light upon a rapidly revolving drum, to which is attached a sensitive photographic film. The source of light now employed by us is a 1000 candle-power "Pointolite," the intensity and steadiness of which enables us to obtain exceedingly good pressure records.

An electrically controlled tuning-fork of 100 vibrations per second is so placed that its beats interrupt momentarily the beam of light

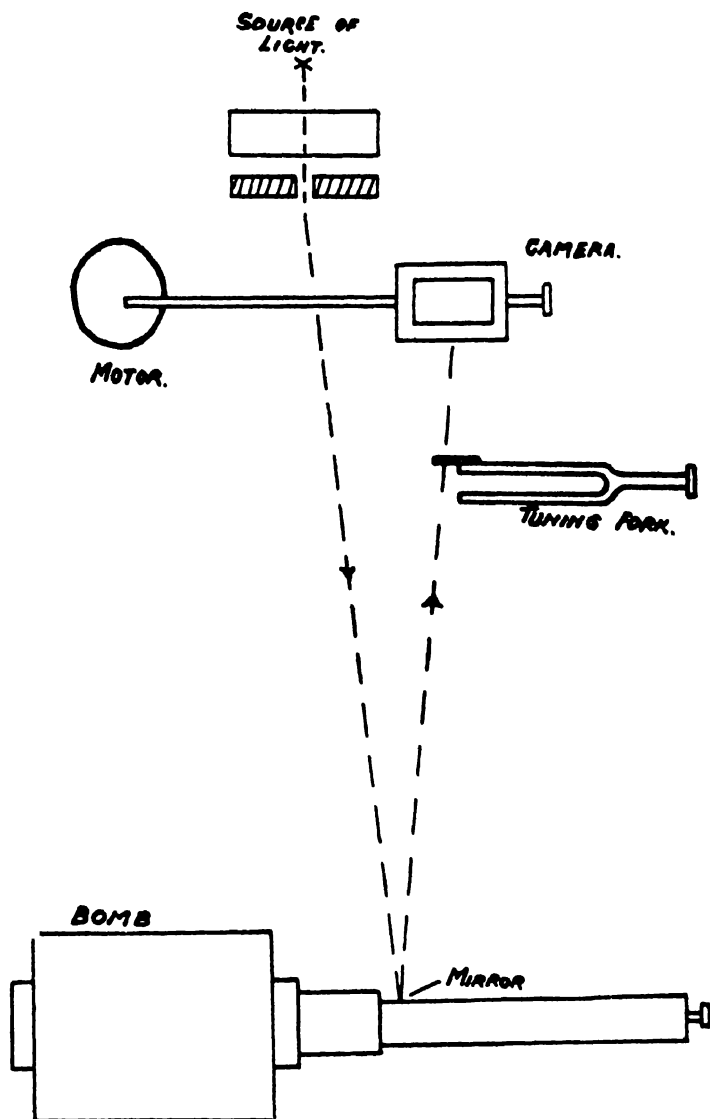


FIG 3.

falling on the photographic film, thus recording a time record on the resulting pressure curve. This is subsequently calibrated by a method that need not be detailed. The intensity of this source of light, and the sensitiveness of the photographic films employed up to now, have enabled us to measure quite definitely 0.005 sec. (or even less) in the pressure-time curves. And in future experiments we hope, with some more sensitive films, to measure the time factor with a

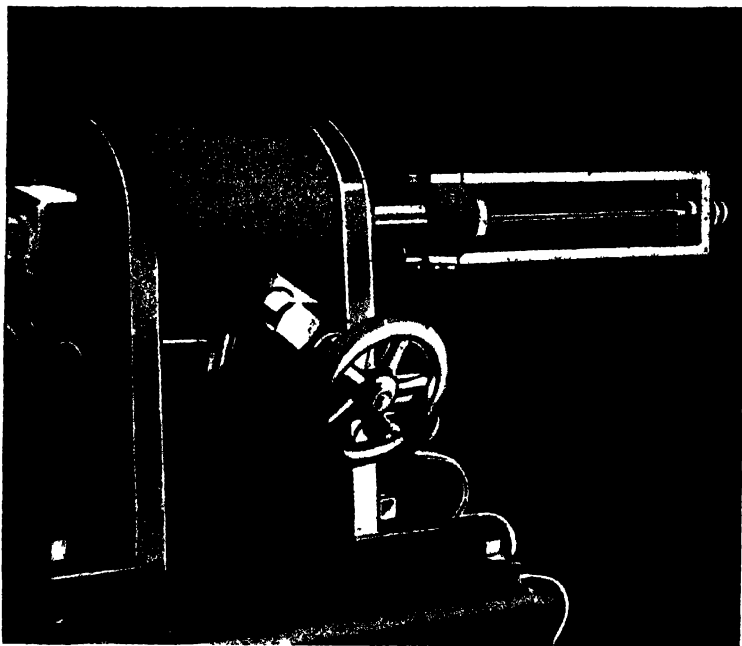


FIG. 4.

still greater degree of accuracy. A photograph of the bomb and gauge, together with the recording arrangements as used in the research, is reproduced in Fig. 4.

As an example of the kind of pressure-time records actually obtained by the foregoing means, we will now throw on the screen a (negative) reproduction (Fig. 5) of a portion of one of our films showing the rising pressure curve obtained when a fast-burning mixture was exploded in the bomb at an initial pressure of 50 atmospheres. You will observe how quickly the pressure rose to a maximum

(somewhat above 400 atmospheres), and then how the cooling period set in immediately afterwards, the time being recorded in hundredths of a second as the beam of light was momentarily interrupted by the beats of the tuning-fork. On the table are exhibited a number of the photographic records obtained in our researches. What such pressure records show chiefly is : (1) the rate at which the potential

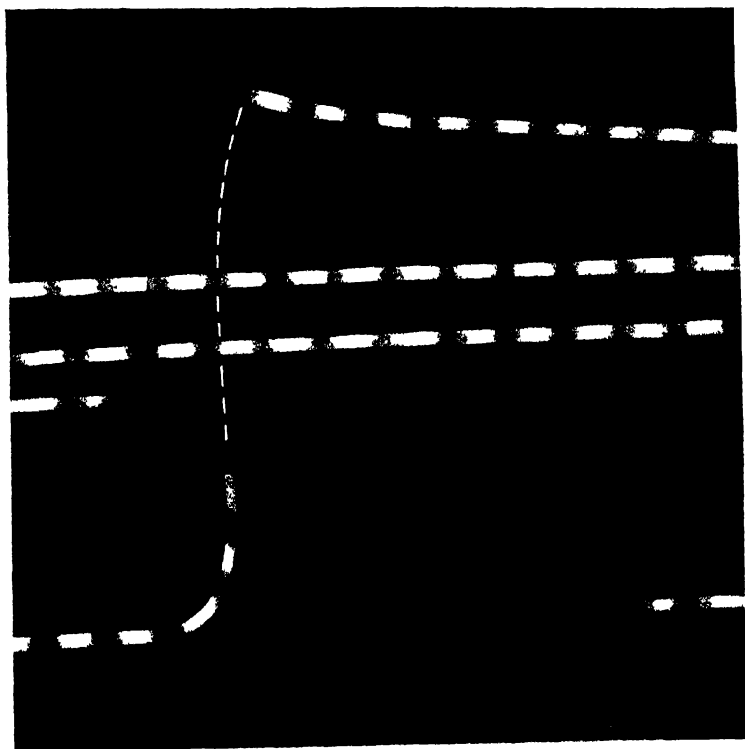


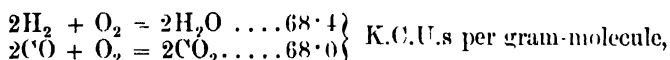
FIG 5

energy of the explosive mixture fired is transferred into kinetic (i.e. pressure or temperature) energy of the products ; (2) the ratio of the maximum pressure attained on explosion to the initial pressure at which the mixture was fired—usually denoted as P_m/P_i ; and (3) the rate of the subsequent cooling. And from a study of these and other features of the records we are able to draw conclusions as to certain fundamental aspects of the combustion process itself.

SOME FEATURES OF THE COMBUSTION OF HYDROGEN AND OF CARBON MONOXIDE IN AIR.

As an example of the potentiality of high-pressure explosion research to reveal and elucidate new factors in gaseous combustion, I propose to deal mainly with the cases of hydrogen and carbon monoxide. For although at first they may seem to be of the simplest type, yet they present features of extraordinary interest and complexity which for many years past chemists have vainly tried to explain. And even engineers, who study internal combustion problems in their own way, without troubling themselves overmuch with the mechanism of the chemical changes involved, are seeking light upon what is termed the "suppression of heat" in such explosions. Indeed, our present ignorance about these matters shows how far we are from really understanding the elements of gaseous combustion, and the need there is of much further fundamental research thereon.

From a chemical standpoint there has always been something enigmatical about the apparently very different behaviours of the two simplest combustible gases, hydrogen and carbon monoxide, when burning in air. For although their volumetric heats of combustion (assuming the initial and final temperatures being both about 15° C) and the proportion by volume in which each of them combines with oxygen are the same, namely :—



yet in many respects their moles of combustion in air present a striking contrast.

Thus, for example, (1) the appearance of a flame of hydrogen in air is very different from the lambent blue flame of carbon monoxide burning at the same orifice and under the same pressure; (2) hydrogen-air mixtures have lower ignition temperatures, and, under similar physical conditions, propagate flame much faster than the corresponding carbon monoxide-air mixtures; (3) the presence of even a minute quantity of steam greatly assists, if it is not absolutely essential to, the oxidation of carbon monoxide in flames, even when detonation is set up—thus a flame of the dry gas is easily extinguished on being introduced into a jar of air that has been previously dried over strong sulphuric acid; (4) a flame of carbon monoxide burning in air loses by radiation nearly 2.4 times as much energy as a hydrogen flame of the same size; also (5) the two radiations have their own characteristic wave lengths—namely, 2.8 μ from a carbon monoxide-air flame and 4.4 μ from a hydrogen-air flame—which have been attributed to vibrational conditions in incipiently formed CO_2 and H_2O molecules respectively, or, as I prefer to say, to the formation *at the moment of combustion* of intensively vibrating carbon monoxide-oxygen and

hydrogen-oxygen complexes, which ultimately give rise to carbon dioxide and steam molecules respectively.

On the table before you are the flames of hydrogen and carbon monoxide respectively, burning side by side in air at the same pressure and orifices of similar diameter, so that you may visualise the striking difference between them. The much slower propagation of flame through normal carbon monoxide-air than through normal hydrogen-air mixtures will next be shown by successively igniting each of them in a vertical glass tube about 20 inches long and $1\frac{1}{2}$ inch in diameter. And, finally, in order to prove how the combustion of carbon monoxide depends on the presence of steam, we will now make the familiar experiment of extinguishing a flame of (dry) carbon monoxide by lowering it into a jar of air which has been previously dried over strong sulphuric acid.

To summarise:—carbon monoxide burns in air more slowly and with a more highly radiating flame than does hydrogen; also apparently the presence of some steam or other hydrogen-containing substance is necessary for its combustion. Precisely how steam accelerates or determines the combustion of carbon monoxide (and only a minute quantity suffices) has up to now never been completely explained; but chemists are generally agreed that carbon monoxide molecules are particularly inert towards oxygen molecules in flames. Indeed I think there are grounds for believing that in ordinary flames carbon monoxide cannot react with undissociated oxygen molecules, but that it requires the presence of either: O atoms or “activated steam”: OH_2 molecules.

HIGH PRESSURE EXPERIMENTS.

Bearing the foregoing considerations in mind, let us now see what new light has been shed on the problem as the result of high pressure combustion research. And here it should be pointed out that, inasmuch as the chief difference between the condition of high and low pressure experiments lies in the absolute concentration of the interacting molecules, it may be expected that factors whose operation chiefly depend on such concentration will become more dominant as the pressure arises. Indeed the value of high pressure work lies in the fact that it tends to show up and accentuate the operation of factors whose influence may be either masked or overlooked at ordinary pressures.

One of the first things we learnt in our experiments was the absence of any direct relation between the rate at which the potential energy of an explosive mixture is transferred on explosion to its products as sensible heat (pressure) and the magnitude of the chemical affinity between its combining constituents. Thus, for example, the time required for the attainment of maximum pressure on exploding at 50 atmospheres a methane-air mixture ($\text{CH}_4 + \text{O}_2 + 4\text{N}_2$), in

which the combustible gas and oxygen are present in equimolecular proportions (i.e. corresponding to the primary chemical interaction in the flame), was many times longer than that required in the case of the corresponding hydrogen-air mixture ($2\text{H}_2 + \text{O}_2 + 4\text{N}_2$), notwithstanding the fact that the affinity of methane is at least twenty, and possibly as many as thirty, times as great as that of hydrogen for oxygen in flames. In other words, the avidity with which a combustible gas seizes upon oxygen in flame combustion is not necessarily the factor which mainly determines the rate at which the potential energy of the mixture is transferred into kinetic energy of its products.

Another thing that came to light during the early stages of our work was that whereas what may be termed "mass influence" of hydrogen upon the actual distribution of oxygen between the combustible constituents of a burning mixture is proportional to the square of its concentration, that of carbon monoxide is nearly proportional to the first power thereof. This can hardly mean otherwise than that whereas the primary oxidation of hydrogen in flames involves the simultaneous action of two H_2 molecules, that of carbon monoxide does not require the action of more than one CO molecule.*

Our later experiments have chiefly dealt with the explosion usually at an initial pressure of 50 atmospheres of what may be termed isothermic mixtures of either carbon monoxide or hydrogen with sufficient oxygen for complete combustion *plus* some variable diluent developing as nearly as may be the same amount of energy on combustion. With the aid of a series of slides showing the character of the pressure curves I will now endeavour to explain their significance.

THE CONTRAST BETWEEN CARBON MONOXIDE-AIR AND HYDROGEN-AIR PRESSURE CURVES.

We may appropriately begin with a consideration of two typical pressure-time records (Fig. 6) obtained when normal carbon monoxide-air and hydrogen-air mixtures ($2\text{CO} + \text{O}_2 + 4\text{N}_2$ and $2\text{H}_2 + \text{O}_2 + 4\text{N}_2$)† were respectively fired in the bomb at an initial pressure of 50 atmospheres.

Now although these two mixtures developed as nearly as may be the same total amount of energy on explosion, there was a striking contrast between the character of the pressure-time curves obtained.

* The experimental evidence for the foregoing statement will be found in Phil. Trans. Roy. Soc., A. 215 (1915), pp. 296-308 and 313-318.

† It should be understood that throughout this discourse the expression a "normal carbon monoxide- (or hydrogen-) air mixture" means a mixture of the combustible gas with the amount of air theoretically required to burn it to carbon dioxide (or steam).

For whereas in the typical hydrogen-air curve the pressure rose with extreme rapidity (actually in 0.005 second) to its maximum (about 400 atmospheres), and almost immediately thereafter began to fall and assume the character of a simple cooling curve, in the correspond-

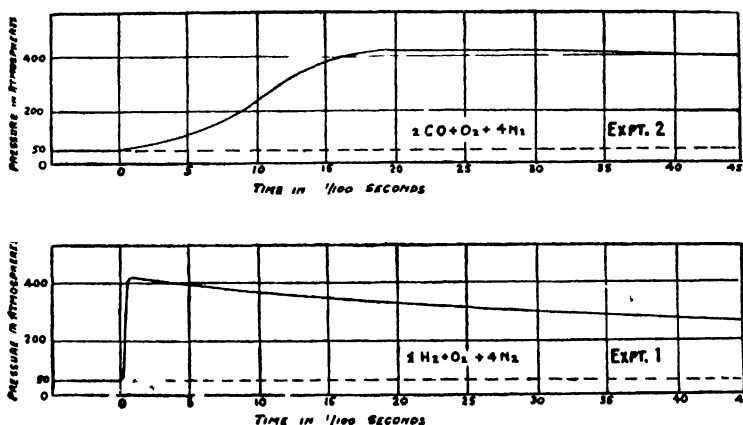


FIG. 6.

ing carbon monoxide curve the pressure rose much more slowly and only attained a maximum (about 410 atmospheres) after 0.18 second, after which it was maintained almost at its maximum for a considerable time interval. The comparative slowness with which pressure energy is developed in such a carbon monoxide-air explosion, together with a considerable exothermic effect after the maximum pressure had been reached, were indeed very remarkable and significant features of our experiments. At first we were inclined to attribute them to the supposed "slow-burning" property of carbon monoxide as compared with the "quick-burning" of hydrogen; but further experiments revealed the operation of another totally unexpected factor—namely, the presence of nitrogen, which, as we discovered later, is not inert but acts as an "energy-absorber" in the combustion of carbon monoxide at such pressures.

EFFECT OF ADDITION OF HYDROGEN UPON THE CARBON MONOXIDE-AIR CURVE AND UPON A CARBON MONOXIDE FLAME BURNING IN AIR.

It was next discovered that the replacement, even in very small proportions, of carbon monoxide by its equivalent of hydrogen in the aforesaid normal carbon monoxide-air mixture had a disproportionately large influence in accelerating the rise of pressure on explosion,

This remarkable result is brought out in the following series of curves (Fig. 7), which show the effects of progressively replacing from one-twenty-fourth up to one-half of the carbon monoxide by its equivalent of hydrogen in the original mixture exploded.

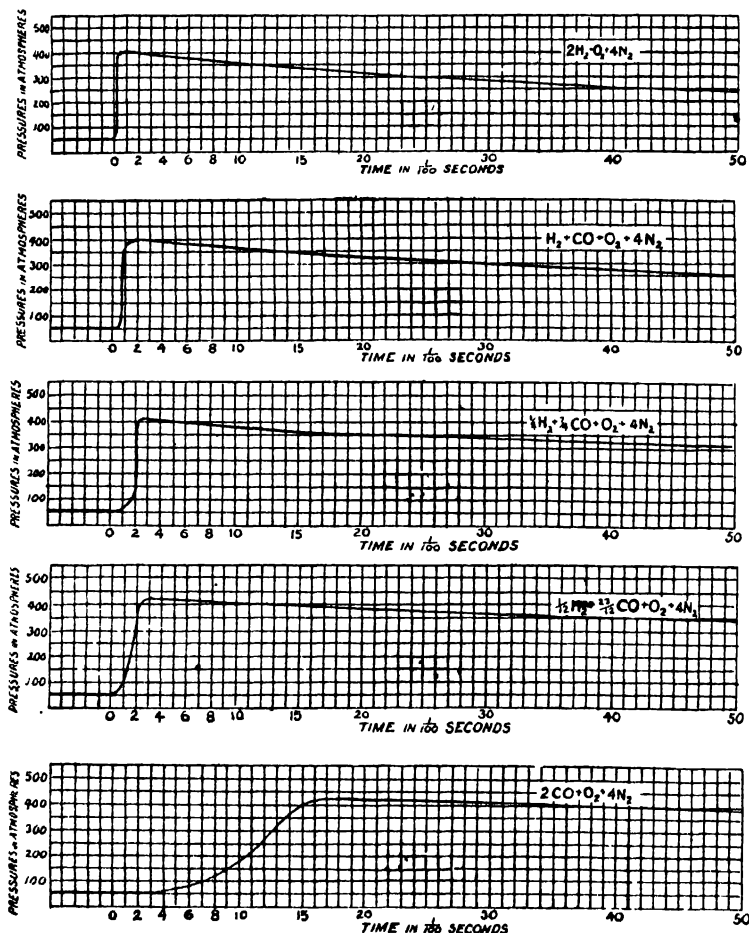


FIG. 7.

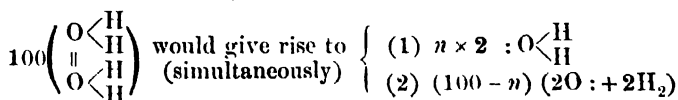
At first sight it seemed as if the hydrogen had imposed its own character upon the whole course of the carbon monoxide combustion, even when the combustible part of the mixture exploded contained only one part of hydrogen to twenty-three parts of carbon monoxide by volume.

In this connection it may be mentioned that the addition of a moderate amount of hydrogen to carbon monoxide burning in air at ordinary pressure has a considerable effect upon the character and spectrum of the flame, a circumstance which seems to be of some significance in relation to the mechanism of carbon monoxide combustion. And in conjunction with Professor A. Fowler, of the Imperial College, we are now investigating it more closely with a view to finding out its meaning. But the facts as now known warrant us in concluding that the addition of a comparatively small proportion of hydrogen has a peculiar influence upon the combustion of carbon monoxide, whether at high pressures (as in our bomb experiment) or in flame combustion at ordinary pressures.

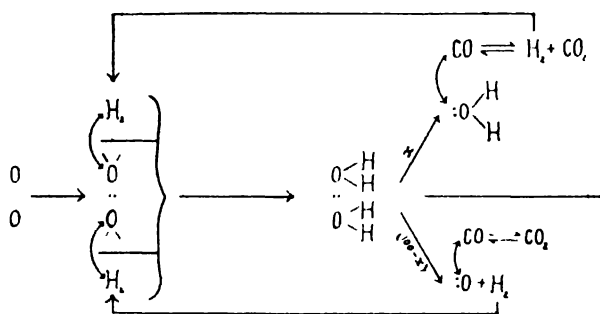
THE MECHANISM OF THE COMBUSTION OF CARBON MONOXIDE.

When the results of our carbon monoxide-hydrogen experiments were published two years ago, I ventured to put forward tentatively the following view of the combustion of hydrogen and carbon monoxide as a basis of discussion, and as it seems to explain most of the known facts, perhaps I may be allowed to refer to it here. It involves the supposition that, whereas in certain cases of combustion (such as that of hydrogen) undissociated O_2 molecules can, and ordinarily do, interact directly with those of the combustible gas, yet in other cases (such as that of carbon monoxide) the dissociation of the oxygen involved is a necessary precedent to the actual oxidation; or in other words, that oxygen in flames may function in two distinct ways, namely, (1) as undissociated O_2 and (2) as atomic : O.

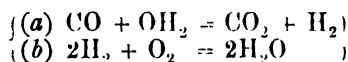
To explain the peculiar influence of hydrogen or steam upon the combustion of carbon monoxide, I think it must be supposed that oxygen and carbon monoxide molecules are mutually inert in flames, and that before the carbon monoxide can be oxidised the O_2 molecules must be resolved either into O atoms or into "activated" steam. This precedent condition can be brought about by the presence of hydrogen (or may be steam) in the mixture undergoing combustion. For, according to my view, an undissociated O_2 molecule on being heated in the flame has its "residual affinities" sufficiently stimulated to enable it to seize upon two hydrogen molecules, forming initially an unstable vibratory complex H_4O_2 . Such a complex, being in an intensely vibratory condition, would instantly break down (1) *partly* into two molecules of steam, also in a vibratory (and therefore "activated") condition, and (2) partly also into two : O atoms and two H_2 molecules, thus : -



The ratio of $n/100 - n$ would obviously depend upon both temperature and environment. The higher the temperature and the less hydrogen in the environment, the less the magnitude of n . But in all conditions the hydrogen in a combustible mixture containing also carbon monoxide functions as a resolver of O_2 molecules simultaneously into (1) "activated" steam and (2) $:O$ atoms. Thus it is suggested that the primary function of hydrogen as a promoter of the combustion of carbon monoxide is to resolve the O_2 molecules (inert towards carbon monoxide) into $:O$ atoms and "activated" OH_2 (reactive towards carbon monoxide), itself being continuously regenerated in the process, as shown in the following scheme :—



It may be observed that this view is similar to the one advanced forty years ago by Professor H. B. Dixon to explain his discovery of the mutual inertness of dry carbon monoxide and oxygen in flames, but modified in one particular so as to make it more applicable to the further facts now known. He supposed that carbon monoxide is oxidised by OH_2 (but not by O_2) molecules in flames, the resulting hydrogen being immediately burnt to steam, which was thus continuously regenerated, as follows :—



If, however, only such interactions (and no others) occur, it is difficult to understand why the colour and spectrum of a flame of pure (moist) carbon monoxide are so unlike those of hydrogen burning in air. The characteristic spectrum of a carbon monoxide flame, which extends far into the ultra-violet, would surely seem to be due to the formation in it of some CO_2 molecules in a more highly vibratory state than would be likely to arise merely by interactions of CO and OH_2 molecules. The difficulty in question is obviated, and also other facts would be better explained, by supposing (as I do) that an unstable vibratory H_4O_2 complex, primarily formed by the

interaction of O_2 and H_2 molecules, decomposes in each of two ways yielding $:OH_2$ and $:O$ atoms, both of which are capable of oxidising carbon monoxide.

It was at the conclusion of this part of our research that the accident happened which so tragically ended poor Haward's life, just as he was commencing another series of experiments designed to develop and follow up the new issues raised. His untimely death cut short a career which had given promise of great distinction in scientific research, to which he was passionately devoted, and bereft us of a colleague whose rare experimental gifts and modest nature were the delight and praise of all who came in contact with him.

THE ENERGY-ABSORBING FUNCTION AND ACTIVATION OF NITROGEN IN THE COMBUSTION OF CARBON MONOXIDE.

From this point onwards the prime object of the research became the elucidation of the carbon monoxide question, and upon this issue all our efforts were now concentrated. It next occurred to us to try the effects of progressively replacing the nitrogen of a normal carbon monoxide ($2CO + O_2 + 4N_2$) mixture by molecular equivalents of other gases, e.g. oxygen, carbon monoxide and argon. The first two of these gases are diatomic, and would have much the same densities and heat capacities as the nitrogen which they replaced; and although they might be expected to exert some "chemical mass" influence upon the combustion, yet in all other respects they would act as "dilutents." In argon we had an absolutely inert monatomic gas of higher density, but smaller volumetric heat capacity, than nitrogen, and incapable of any internal vibrational energy. It would therefore presumably be incapable of exerting any effect upon the explosion other than that of merely sharing, by molecular collisions, in the increased kinetic energy acquired by the system as the result of the combustion.

It may be observed that whilst the said replacement of the nitrogen by the other gases would not effect in any way the total energy liberated on explosion, yet the experiments showed that it affected somewhat the proportion of the energy recorded by the gauge as pressure (temperature) at the instant of maximum pressure, and still more so the rapidity with which the said pressure energy was developed.

In order not to embarrass you with more experimental detail than is necessary to illustrate the most salient features of our results, reference to a large number of intermediate experiments may be omitted, and attention focused upon those in which the replacement of nitrogen by the other gases was complete.* The most important

* Full details of these have been published in the Proc. Roy. Soc., A. 108 (1923), pp. 205 to 232.

experimental results from this point of view are summarised in Table I., and illustrated by the set of pressure-time curves reproduced in Fig. 9. And here it may be pointed out that the most essential data which must be established in such experiments are the following :—

P_i = the initial pressure in atmospheres at which each mixture is fired.

P_m = the maximum pressure in atmospheres recorded in the explosion.

t_m = the time in seconds required for the attainment of the maximum pressure after ignition.

Σ = the thermal equivalent in K.C.U.s of the energy liberated during the explosion.

Also the percentage amount by which P_m falls during (say) 0.5 sec. after t_m .

TABLE I.

Mixture Exploded	Σ	P_i	t_m	P_m	P_{11}/P_i	% Fall in Pressure in 0.5 sec. after t_m
$2\text{CO} + \text{O}_2 + 4\text{N}_2$	10.2	50	0.190	409	8.18	11.6
$2\text{CO} + \text{O}_2 + 4\text{O}_2$	10.0	50	0.005	460	9.20	33.33
$2\text{CO} + \text{O}_2 + 4\text{CO}$	10.4	50	0.010	450	9.00	34.3
$2\text{CO} + \text{O}_2 + 4\text{Ar}$	10.2	50	0.025	510	10.20	26.4

These and other similar results brought home to us very forcibly the conclusion that the nitrogen present in the normal carbon monoxide-air mixture had been exerting a specific influence on the whole course of events, which was manifested in a three-fold effect upon the pressure curves—namely, (1) a marked retardation of the rate of attainment of maximum pressure, (2) a lowering of the maximum pressure, and (3) a considerable retardation of the subsequent cooling. For whenever such nitrogen was wholly replaced by its molecular equivalent of any one of the other three gases, the development of pressure became nearly as rapid as in the explosion of a normal hydrogen-air mixture under like conditions. Moreover, comparative analyses of the pressure-time records obtained during the experiments in question have shown that, when nitrogen was present, much less kinetic (pressure) energy was absorbed up to the attainment of maximum pressure than was subsequently liberated during the cooling period. This remarkable circumstance shows that a considerable part of the radiation emitted by the burning carbon monoxide (which otherwise would have been absorbed by the walls of the

explosion vessel) was intercepted by the nitrogen present. Part of the nitrogen so irradiated would then, in favourable circumstances, be oxidised to nitric oxide, thereby absorbing part of the kinetic energy developed by the explosion and consequently reducing the maximum pressure attained. Finally, the radiant energy so absorbed

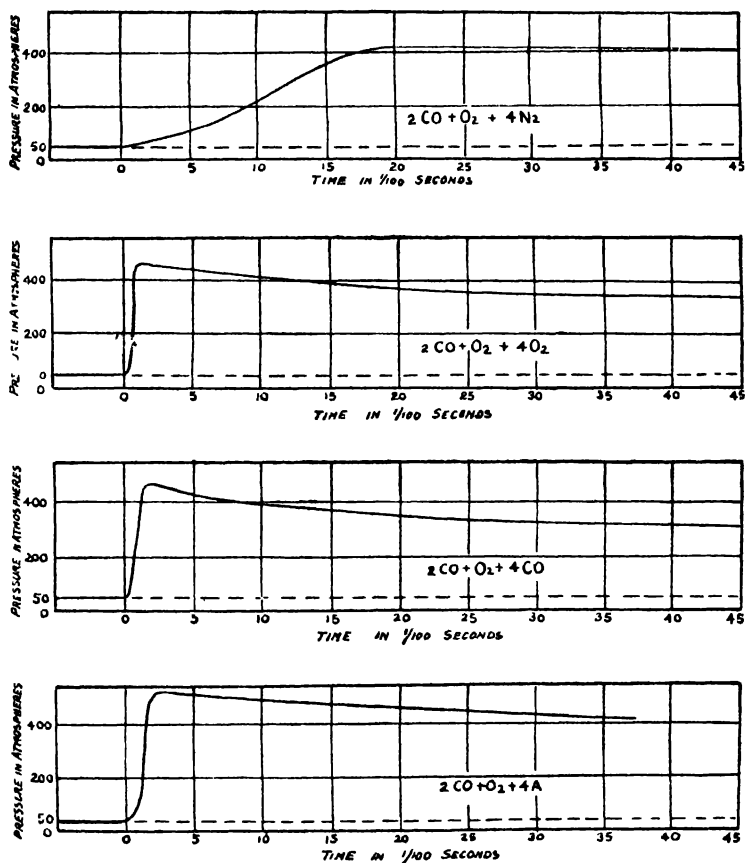


FIG. 8.

by the nitrogen, *plus* part of the kinetic energy (if any) absorbed in forming nitric oxide during the combustion, was liberated as kinetic energy during the cooling period, so delaying the cooling. Thus it was manifest that, under our experimental conditions, nitrogen has the power of absorbing part of the radiant energy developed by the combustion of carbon monoxide, and of slowly giving it out again in

a kinetic form during the subsequent cooling period. In other words, nitrogen is not inert, but acts as an "energy absorbing" spring in such explosions. Indeed the results set forth in Table I. can hardly be explained on any other supposition.

Another important conclusion arising out of these experiments is that when nitrogen so absorbs radiant energy developed during a carbon monoxide-air ($2\text{CO} + \text{O}_2 + 4\text{N}_2$) explosion under such conditions, it becomes chemically "activated," and capable of combining much more readily with oxygen than does nitrogen which has merely been raised to a correspondingly high temperature in a similar hydrogen-air ($2\text{H}_2 + \text{O}_2 + 4\text{N}_2$) explosion. Indeed, when the bomb was rinsed out with distilled water after one of our hydrogen-air explosions at an initial pressure of 50 atmospheres, no more than a faint trace of nitric acid could be detected on applying the diphenylamine test to the washings; whereas in the case of the corresponding carbon monoxide-air explosions, a similar test always showed a considerable formation of nitric acid.

It would seem as though the nitrogen molecule is able to absorb the particular quality of radiation emitted as the result of the interactions of CO and :O during a carbon monoxide-air explosion, which is different from that emitted during a hydrogen-air explosion. In other words, it seems as though there is some constitutional correspondence between CO and N_2 molecules (whose densities are identical) whereby the vibrational energy (radiation) emitted when the one burns is of such a quality as can be readily absorbed by the other, the two thus acting in resonance. The radiant energy so absorbed during the explosion presumably would not affect the maximum pressure attained, except in so far as the conditions permitted of any secondary oxidation of the "activated" nitrogen to nitric oxide during the actual combustion period; but radiant energy so absorbed would be liberated in a kinetic form during the subsequent cooling period, as the "activated" nitrogen slowly reverted to the ordinary form. And analyses of the pressure-time records obtained have confirmed this supposition.

Perhaps the following graphs (Fig. 9) will enable you to appreciate the strength of the evidence obtained up to this point as to the activation of the nitrogen during a carbon monoxide-air explosion at high pressures.

They show the rates of cooling (expressed as pressure fall in atmospheres per second) of the gaseous systems immediately after the attainment of maximum pressure, when each of the four mixtures $2\text{CO} + \text{O}_2 + 4\text{N}_2$, $2\text{CO} + \text{O}_2 + 4\text{O}_2$, $2\text{CO} + \text{O}_2 + 4\text{Ar}$, and $2\text{H}_2 + \text{O}_2 + 4\text{N}_2$ were exploded in the bomb at an initial pressure of 50 atmospheres. It will be seen that, except in the case of the carbon monoxide-air mixture, the cooling was perfectly regular, and presented no abnormal features whatever. In the case of the $2\text{CO} + \text{O}_2 + 4\text{N}_2$ mixture, however, there was no cooling at all during

the 0.1 sec. after the attainment of the maximum pressure; and it was not until the lapse of the 0.6 sec. thereafter that anything like a normal rate of cooling was established. Attention is specially drawn to the striking contrast between the perfect normality of the first 0.6 sec. of the cooling period in the case of the hydrogen-air ($2\text{H}_2 + \text{O}_2 + 4\text{N}_2$) mixture, and its complete abnormality in the case of the corresponding carbon monoxide-air mixture. This circumstance, combined with the perfect normality of the cooling in the case of the $2\text{CO} + \text{O}_2 + 4\text{Ar}$ mixture, can hardly be explained except on the assumption that the nitrogen functions differently in a

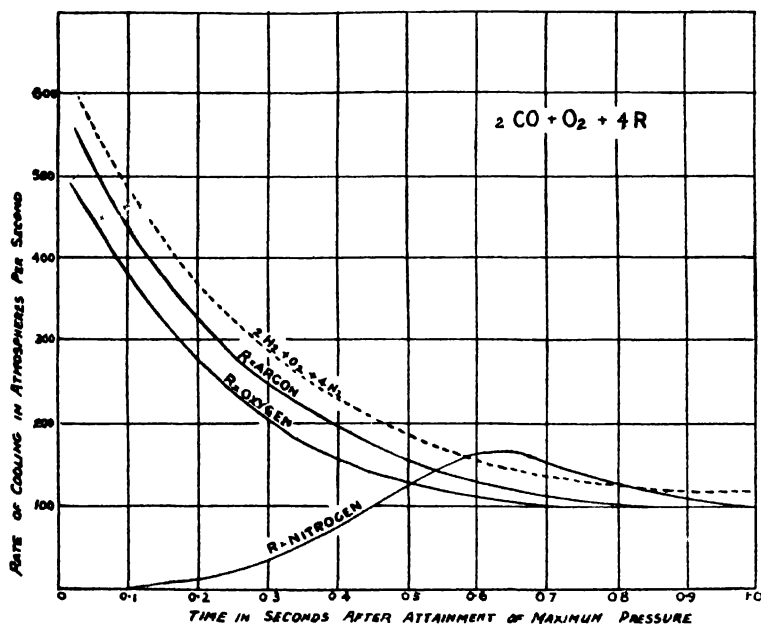


FIG. 9.

hydrogen-air explosion, where it acts as an inert diluent only, from what it does in a carbon monoxide-air explosion, where in addition to its ordinary diluent action it has a peculiar "energy absorbing" effect, whereby it becomes chemically "activated." On such an assumption the meaning of the $2\text{CO} + \text{O}_2 + 4\text{N}_2$ cooling curve is that the radiant energy which had been absorbed by the N_2 molecule during the previous combustion period was being slowly evolved in a kinetic form far into the subsequent cooling period, the "activated" nitrogen not having entirely reverted to its normal condition until at least 0.6 sec. after the end of the combustion period

EXPERIMENTS WITH ISOTHERMIC MIXTURES $2\text{CO} + \text{O}_2 + n\text{R}$
(WHERE $n = 0, 2, 4$ OR 6 , AND $\text{R} = \text{Ar}, \text{CO}, \text{O}_2$ OR N_2).

Let us now pass on to consider (1) the behaviour of an *undiluted* mixture of carbon monoxide and oxygen in their combining proportions ($2\text{CO} + \text{O}_2$) on explosion in the bomb at a pressure (21.4 atmospheres) such that the total energy liberated would be nearly the same as in all the other experiments in so far referred to; and (2) the effect of adding thereto successive molecular proportions (2, 3, 4 and 6) of one or other of the four diluents R (i.e. $\text{Ar}, \text{CO}, \text{O}_2$ and N_2).

The pressure-time records obtained when the undiluted $2\text{CO} + \text{O}_2$ mixture was exploded at the said initial pressure is shown in Fig. 10, from which it will be seen that the maximum pressure (245 atmospheres) was developed in 0.005 sec., after which the cooling period immediately set in; the pressure fall during the next 0.5 sec. being 66 atmospheres, or about 27 per cent. of the maximum. It is evident that an exceedingly high temperature was momentarily attained in this experiment; indeed, assuming that the "chemical contraction" involved in the passage from $2\text{CO} + \text{O}_2$ (3 vols.) to 2CO_2 (2 vols.) was substantially completed at the instant of maximum pressure, the temperature at that instant would have been of the order of 5000°C . In any case the experiment finally disposes of the supposition that carbon monoxide is inherently a "slow burning" gas. Moreover, the whole character of the pressure-time curve seems inconsistent with the idea, which has sometimes been put forward, that the maximum pressure attained on explosion is materially affected by the dissociation of carbon dioxide; indeed, there was no sign of any "after burning" or heat evolution after P_m had been attained.

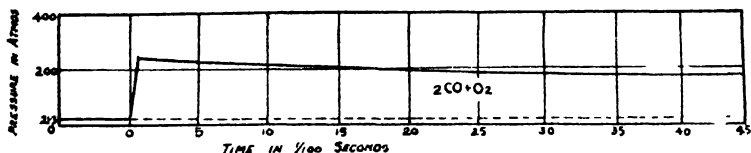


FIG. 10.

The effect of diluting the theoretical mixture $2\text{CO} + \text{O}_2$ with successive molecular proportions of R may be judged from Table II., which is almost self-explanatory. The following features are, however, perhaps the most noteworthy: -

When $n = 2$. There was no perceptible retardation in the rate of attainment of maximum pressure so long as either carbon monoxide or oxygen was the diluent, from which it may be inferred that their

TABLE II.—RESULTS OF EXPERIMENTS WITH MIXTURES $2CO + O_2 + nR$ (WHERE n WAS VARIED AND $R = Ar, CO, O_2$ OR N_2).

Expt. No.	Approximate mixture	Percentage composition of mixture				Initial temp., t_m (secs.)	Pressure in atmospheres			Ratio $\frac{P_m}{P_f}$
		CO	O_2	N_2	Ar		P_i	P_m	P_f (corr.)	
22	$2CO + O_2$	64.38	32.03	3.59	—	18.0	21.4	245	14.2	9.9
23	$2CO + O_2 + 2Ar$	39.65	19.37	—	40.98*	15.8	35.7	380	28.5	10.3
24	$2CO + O_2 + 2O_2$	39.10	57.04	3.26	—	17.8	35.7	368	28.4	10.1
25	$2CO + O_2 + 2CO$	75.01	20.89	4.10	—	17.2	35.7	360	28.4	10.6
26	$2CO + O_2 + 2N_2$	40.38	19.89	39.73	—	16.6	35.7	340	28.3	10.3
21	$2CO + O_2 + 4Ar$	28.67	14.45	—	56.98*	17.5	50.0	510	42.72	10.4
9	$2CO + O_2 + 4O_2$	28.36	67.91	3.73	—	18.4	50.0	460	42.70	10.1
15	$2CO + O_2 + 4CO$	80.98	14.76	4.26	—	16.5	50.0	450	42.51	10.6
16	$2CO + O_2 + 4N_2$	28.48	14.27	57.25	—	15.6	50.0	415	42.62	10.3
27	$2CO + O_2 + 6Ar$	23.11	10.89	—	66.00*	17.8	64.3	620	57.7	10.0
28	$2CO + O_2 + 6CO$	89.40	12.33	4.27	—	18.2	64.3	510	57.6	11.3
29	$2CO + O_2 + 6N_2$	23.41	11.11	65.48	—	16.8	64.3	410	56.9	10.3

* N_2 in mixture would be about 2 per cent

purely "diluent" effects were just counterbalanced by their opposite "chemical mass" effects. Dilution with argon increased t_m from 0.005 to 0.010 sec., which may be considered as a purely diluent effect, whereas in the corresponding experiment with nitrogen it was drawn out to 0.04 sec. The "energy absorbing" influence of nitrogen as compared with either of the other diatomic gases is well brought out by the results, the radiant energy so absorbed during the combustion being slowly liberated in a kinetic form during the subsequent cooling period, which was thereby considerably retarded.

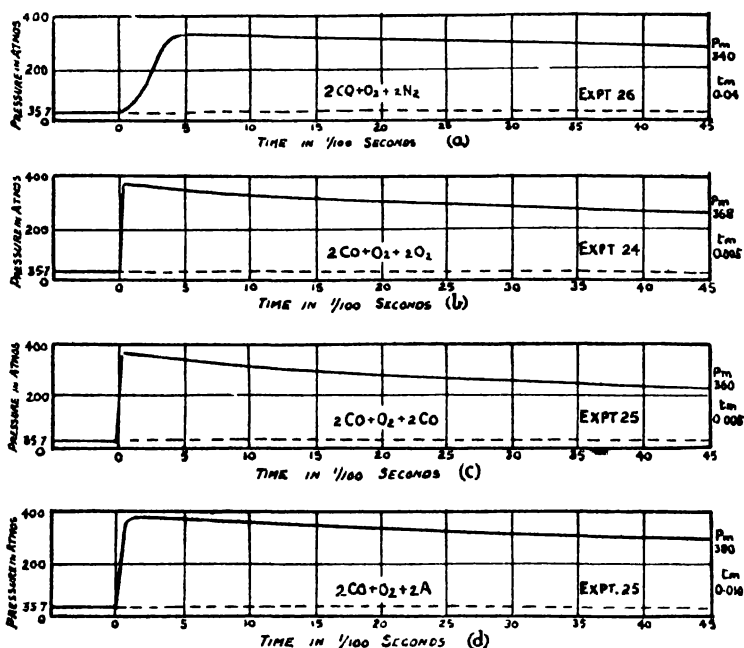


FIG. 11

When $n = 1$. The further retardation in the attainment of P_m when more argon was added was just what might have been expected with a purely "diluent" gas. The "chemical mass" influence of the additional carbon monoxide or oxygen upon t_m is again very manifest, but with nitrogen as the diluent t_m becomes as long as 0.190 sec. The "energy absorbing" effect of nitrogen during the combustion has now become very marked, and the liberation in a kinetic form of the energy so absorbed was traceable far into the cooling period.

When $n = 6$. A point has now been reached when the "chemical mass" effect of the additional carbon monoxide or oxygen upon t_m were largely counterbalanced by their "diluent" effects, and especially was this so in the case of oxygen. But the most striking feature of all is the "energy absorbing" influence exerted by the $6N_2$ diluent, which caused the t_m to be drawn out to as long as 1.100 sec. Also the ratio P_m/P was reduced from the 7.9 obtained with the $6CO$ as diatomic diluent of the same density to 6.4 , or by nearly 20 per cent.—a result that speaks for itself. These features are all well brought out in the following pressure-time curves (Fig. 12).

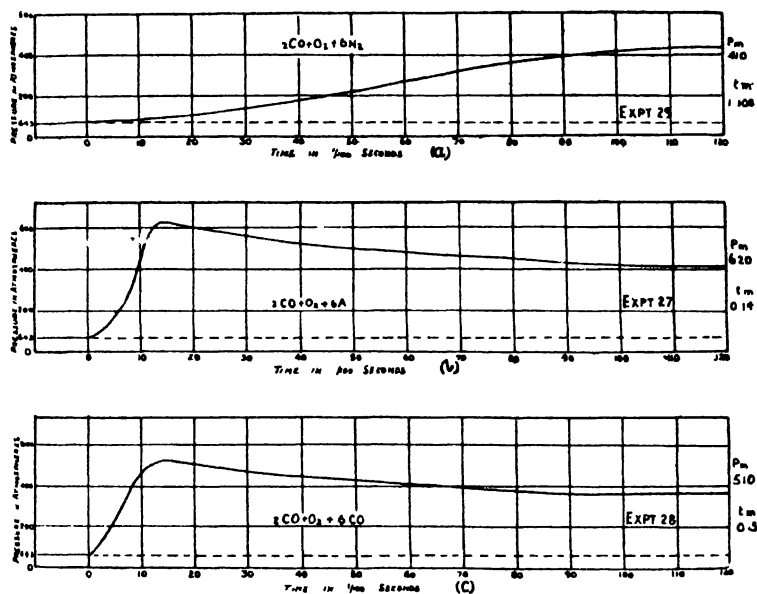


FIG. 12.

Perhaps the following graphs (Figs. 13 and 14), which show the influence of the successive dilutions in question upon t_m and the observed ratios P_m/P , respectively, will help you to grasp the significance of this part of the experimental evidence. In Fig. 13 are plotted as abscissae the values of t_m in seconds against the R-diluent concentration as ordinates ($n = 2, 3, 4$ and 6 respectively), except that the $6O_2$ and $6N_2$ values are not shown, the last-named ($t_m = 1.100$ sec.) because it would have come much too far away on the right-hand side of the diagram to be included in it.

It should be noted (1) how the "chemical mass" effect of the excess carbon monoxide or excess oxygen predominates over the

"diluent" effects up to $n = 4$; and (2) how at all corresponding dilutions nitrogen retarded the attainment of maximum pressure much more than did the inert diluent argon.

In Fig. 14 are plotted as ordinates the observed values P_m/P_0 against the R-diluent concentrations as abscissæ ($n = 0, 2, 4$ and 6 respectively), and perhaps a few words about the significance of the differences between the argon ordinates and those of the other diluents at corresponding concentrations may be helpful here.

The energy of a gaseous system such as we are considering is of course comprised partly of translational motions of its molecules as a whole, and partly of motions of some kind internal to these molecules.

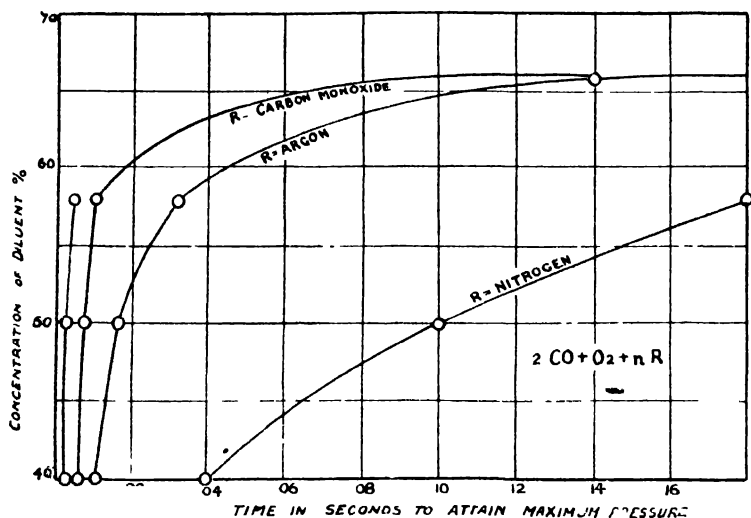


FIG. 13.

The former causes pressure (temperature), but the latter (which according to circumstances may be partly rotational and partly vibrational) produces no external physical effect other than radiation, which originates in high frequency vibrations within the molecule.

Now, in each of the experiments in question a definite amount of energy (thermally equivalent to about 10 K.C.U.s) was liberated by the union of carbon monoxide and oxygen in the bomb. Presumably the greater part of this would appear as increased kinetic energy of the products as a whole (i.e. as pressure). And inasmuch as an increase in the mean translational motion of the molecules of either carbon dioxide or any diatomic diluent implies also some corresponding increase in their internal rotational energy, but not so in the case of

monatomic gas such as argon, it therefore follows that the difference between the argon diluent ordinates and those of the carbon monoxide or oxygen diluent experiments at corresponding concentrations may be regarded as substantially representing the increased intra-molecular "rotational" energy of the two last named. In the case of the nitrogen-diluent experiments, the observed ordinates are subject to a "cooling correction" before they are strictly comparable with the others, because of the longer times always taken to attain the maximum pressure. But even when so "corrected," they would show a

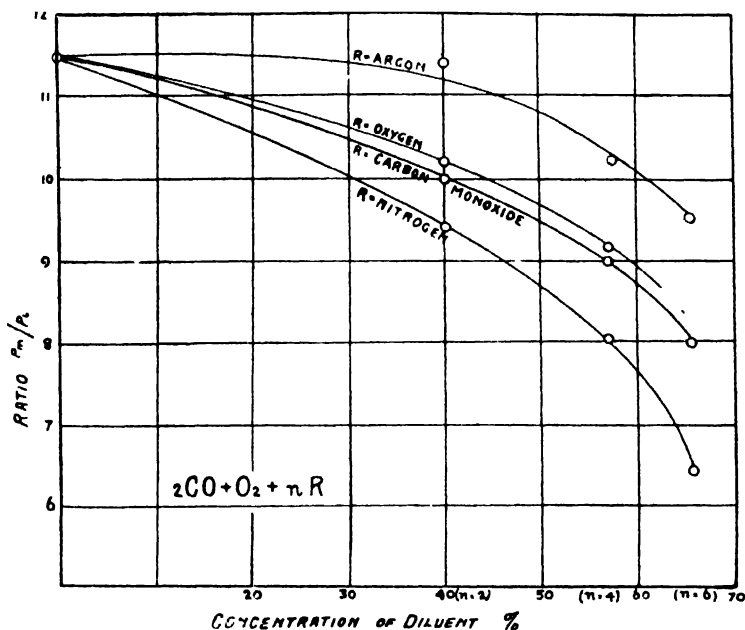


FIG. 14.

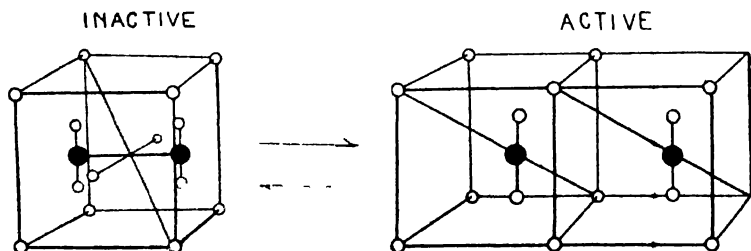
decided absorption of kinetic energy during the combustion period, which may be attributed to the secondary formation of some nitric oxide from the "activated" nitrogen primarily formed.

The lesser part of the energy liberated in explosions would manifest itself as "radiation" of wave lengths characteristic of burning carbon monoxide—i.e. of incipiently forming carbon dioxide molecules in a highly vibrating state such as would result from CO and :O collisions. Now when nitrogen is present as a diluent it is able to intercept part of the "radiation" whereby it acquires energy of a vibrational kind, which may be intense enough even to dissociate the two atoms of its molecule, and in any case "activate"

it chemically. Such an absorption of radiant energy presumably would not affect the ratios P_m/P_i , except in so far as any part of the nitrogen primarily "activated" successfully competed with the burning carbon monoxide for the available oxygen, and thus became oxidised to nitric oxide during the combustion period. Indeed further experiments (now proceeding) have shown that such nitrogen "activation" is materially influenced by the initial pressure at which the explosive mixtures are fired; but this is an aspect of the matter which time does not permit me to follow up to-night.

There is of course nothing new in the idea of an "active" form of nitrogen, for ten years ago the Hon. R. J. Strutt (now Lord Rayleigh) discoursed upon it in this room, and showed how ordinary nitrogen is chemically "activated" when subjected at low pressures to a Leyden jar discharge, whereby it glows and acquires the power of combining with various substances towards which it is normally inert. Such "active" nitrogen was found to be strongly endothermic, and Strutt favoured the view that it consists of dissociated nitrogen atoms, when recombination to ordinary nitrogen caused the characteristic after-glow.*

Another view of the "activation" of nitrogen has been suggested which does not necessitate the complete dissociation of nitrogen molecules. According to Langmuir's statical representation of atomic constitution, there is a great similarity between the configuration of carbon monoxide and nitrogen molecules in the ordinary state, a circumstance to which he has drawn special attention. He considers that both molecules are capable of existing in two forms, in one of which (the ordinary and more inert form) the two positive nuclei are both symmetrically located within one and the same outermost shell of eight electrons, whereas in the "active" form they are situated each within one of two separate shells, which have four electrons in common. According to this view not only would the "activation" of each gas be brought about by a reversible transformation from the one configuration into the other, e.g.



but also an inert nitrogen configuration should be capable of being

* Proc. Roy. Inst., vol. xx. part 3 (1914), pp. 656-661.

activated through resonance with a carbon monoxide molecule of similar configuration undergoing combustion.

It is interesting now to recall the following passage from one of Faraday's letters to Schönbein, which was quoted by the Hon. R. J. Strutt (now Lord Rayleigh), when lecturing in this place on "Active Nitrogen" ten years ago: "What of nitrogen? Is not its apparent quiet simplicity of action all a sham? Not a sham, indeed, but still not the only state in which it can exist. If the compounds which a body can form show something of the state and powers it may have when isolated, then what should nitrogen be in its separate state?" Perhaps the behaviour of nitrogen in our high-pressure carbon monoxide-air explosions will help you to realise more fully the deep significance of Faraday's words.

In the earlier part of my discourse I drew your attention to the peculiar influence of a small addition of hydrogen to a carbon monoxide-air mixture undergoing combustion whether at atmospheric pressure or when exploded at high pressures in the bomb. We have also found that a similar small addition of hydrogen to a normal carbon monoxide-air mixture undergoing combustion at high pressures is prejudicial to the "activation" of nitrogen. This is a point of considerable theoretical as well as practical interest; and had the time permitted, I would have liked to have enlarged upon its significance, and to explain how well it harmonises with the views which I have put forward respecting the mechanism of carbon monoxide combustion.

Leaving the many theoretical issues raised by our experiments to be settled by a further appeal to facts as the investigation proceeds, I perhaps may be permitted to indicate in conclusion one or two directions in which, if followed up with adequate means and resources, the work might lead to results of further interest.

In the first place, we have already in some of our experiments attained extraordinarily high temperatures; and we could go even higher were it not for the fact that we are approaching the safety limits of the bomb. If funds were forthcoming for the construction of a new bomb, with the necessary accessories, to enable us to work at still higher initial pressures than we have hitherto employed, we should be able to study the effects of subjecting small quantities of diluent gases to the combined influence of exceedingly high temperatures and intensive radiation. This is an aspect of the research which we are hoping it may be possible for us to pursue in the interests of Science.

It is also obvious that our results may have considerable bearing upon the problem of nitrogen fixation. For, having proved that nitrogen can be activated by the combustion of carbon monoxide at high pressures, especially when hydrogen is as far as possible excluded from the system, we have in blast furnace gas an almost unlimited supply of just the right kind of raw material from which undoubtedly

nitric acid could be easily produced under the conditions indicated by our experiment. And in view of the national importance of nitrogen fixation, we hope these possibilities will be thoroughly explored at home, and not left entirely to foreign organisations, who will probably not be slow to seize upon them.

I trust that enough has been said to convince you that high pressure combustion work is opening up new possibilities of extending our knowledge, and that however much chemical research may have taught us concerning flame and combustion since the time of Davy, there remains a vast amount still to be learnt.

[W. A. B.]

Friday, May 18, 1923.

SIR ALFRED YARROW, Bart., F.R.S. M.Inst.C.E.,
Manager and Vice-President, in the Chair.

W. M. MORDEY, Past-Pres. I.E.E., M.Inst.C.E., M.R.I.

Some New Effects of Alternating Magnetism.

AN alternate-current electro-magnet behaves very like a permanent magnet, or a direct-current electro-magnet, when presented to a mass of iron filings or to any other ordinary magnetic material in a finely divided state,rafts of the material adhering to the poles and joining them if they are not too far apart. But the use of an alternate-current magnet for such ordinary purposes of attraction does not offer any advantage over ordinary electro-magnets; on the contrary, it is generally less convenient and involves a greater expenditure of energy, and at a low-power factor.

But if we carry our experiments further, we come across some effects which may be of interest.

Let us make some direct comparisons.

We take two electro-magnets of the same size, one excited by direct current, and the other by alternate current of equivalent amount, both with laminated cores. On dipping them successively in masses of ordinary magnetic materials in the form of filings or powder,* the direct-current magnet picks up a rather greater weight than the alternate-current magnet, but otherwise there is no marked difference. This we find is the result with iron filings, nickel filings, cobalt powder, magnetite (the magnetic oxide of iron, Fe_3O_4), and with the Heusler alloy, that interesting magnetic alloy of three non-magnetic metals, copper, manganese and aluminium.

We then try specular haematite, the black crystalline form of ferric oxide Fe_2O_3 , which is usually described as very feebly magnetic. It does not adhere to either magnet.

* The materials must be used in a finely divided form to prevent eddy currents being produced in them by alternating magnetism, and for a similar reason the core of the alternate-current electro-magnet must be laminated. It would be well if all electro-magnets for laboratory use were laminated, as they could then be used for either direct or alternate current.

Let us now place the two magnets with their poles upward, and in succession sprinkle a little of the powdered materials on glass plates over the poles. We find that the iron, nickel, cobalt, magnetite, and the Heusler alloy, all form lines of force of the usual magnetic or "axial" character over either the direct current or the alternate-current magnet.

As examples, Figs. 1, 2, and 3 show respectively the lines of force formed over alternate-current magnets by loadstone—a variety of magnetite—by cobalt, and by the Heusler alloy. (The magnets used in these three cases were of different shapes.)

So far there is nothing unexpected.

But when we try the specular hæmatite sprinkled on a glass plate we get a very different result. Over the direct-current magnet there is a hardly perceptible orientation immediately over the pole, but no other movement and no formation of lines of force. Over the alternate-current magnet, however, when the plate rests on the pole a very small amount of the material is attracted to the pole, but most of it is repelled briskly, in all radial directions, forming a distinct ring or halo about 8 inches inside diameter, as seen in Fig. 4. On slightly raising the plate, or weakening the field, the small amount of attracted material is repelled, joining the halo.

(The magnet in this case was a bar magnet made up of strips of thin sheet-iron, the section being about half a square inch.)

On examining this halo through a magnifying glass we find no sign of any lines of force either circular or radial. The positions of the particles indicate that they have no attraction for one another, indeed mutual repulsion is suggested. On scattering some more of this material over the poles of a horseshoe alternate-current magnet, we get the formation shown in Fig. 5, two halos—one round each pole—coalescing to form a very clear line, across or at right angles to the direction of ordinary magnetic lines of force. On slightly raising the plate a little material clustered about the poles was repelled, joining the halos. As in the previous case, except for the halo formation, there is no sign of order or of lines of force amongst the particles, nor is anything of the sort visible even with the magnification of a lantern slide.

Our attention is arrested by the behaviour of the very small amount of the material that happens to be close to the poles: by the fact that it is feebly attracted when near the poles—that is, when in a strong field; and is repelled when not so near the poles—that is, when in a weaker field. Most of the material sprinkled over the glass, being in a weak field, is repelled from the poles.

When the material is placed only over the poles a position of the plate may often be found where neither attraction nor repulsion appears to take place—at less than that distance from the poles there is attraction, at a greater distance there is

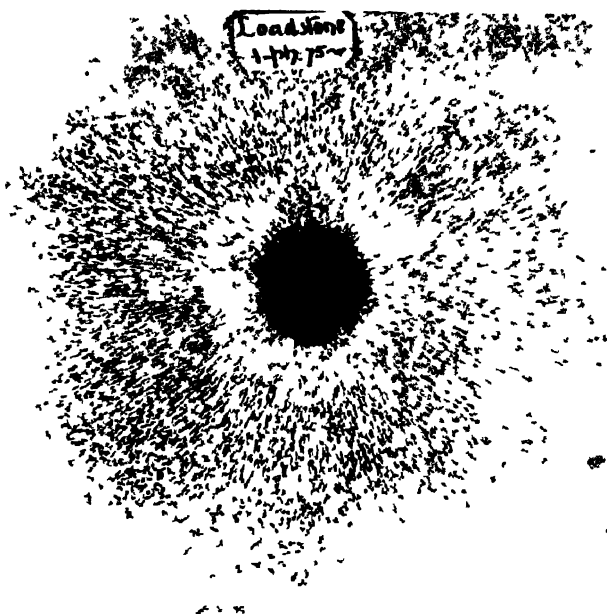


FIG. 1.—POWDERED LOADSTONE OVER ONE POLE OF AN ALTERNATE CURRENT BAR MAGNET, 1 PHASE

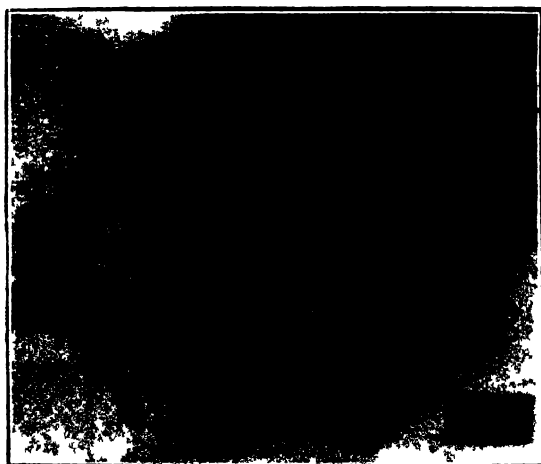


FIG. 2.—COBALT OVER THE POLES OF AN ALTERNATE CURRENT HORSESHOE MAGNET, 1 PHASE



FIG. 3.—HEUSLER ALLOY OVER THE POLES OF AN ALTERNATE-CURRENT HORSESHOE MAGNET, 1-PHASE.

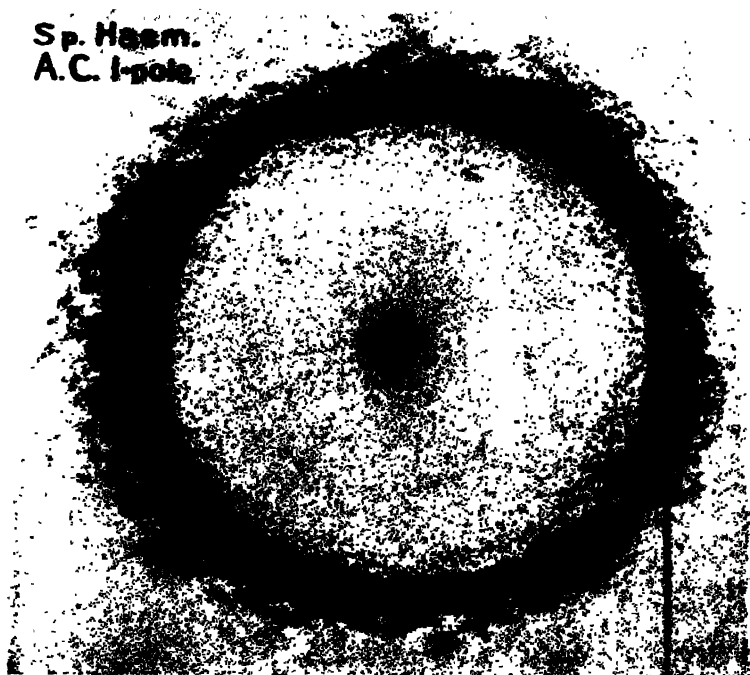


FIG. 4.—SPECULAR HÆMATITE HALO OVER ONE POLE OF AN ALTERNATE-CURRENT BAR MAGNET, 1-PHASE.

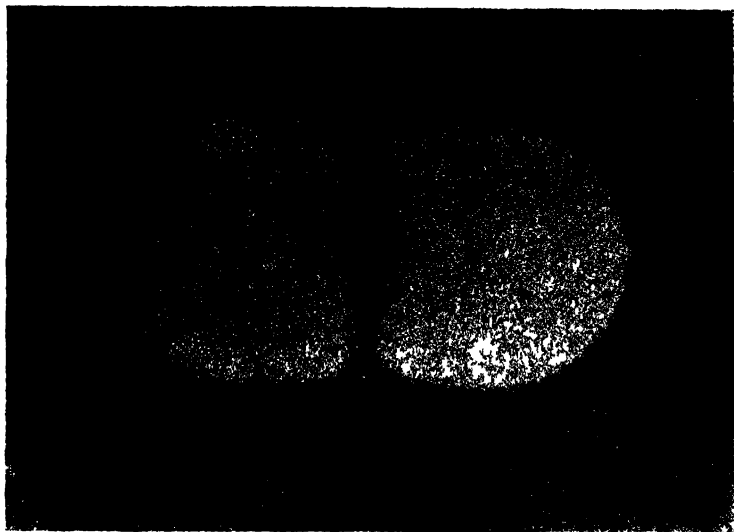


FIG. 5—SPECULAR HEMATITE HALOS OVER THE POLES OF AN ALTERNATE CURRENT HORSISHOE MAGNET 1 PHASE

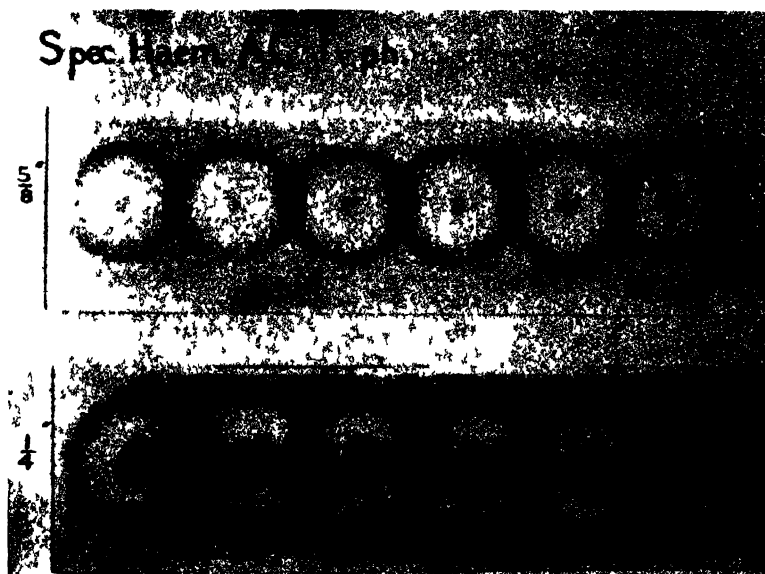


FIG. 6—SPECULAR HEMATITE HALOS OVER A MULTIPOLAR MAGNET 1 PHASE

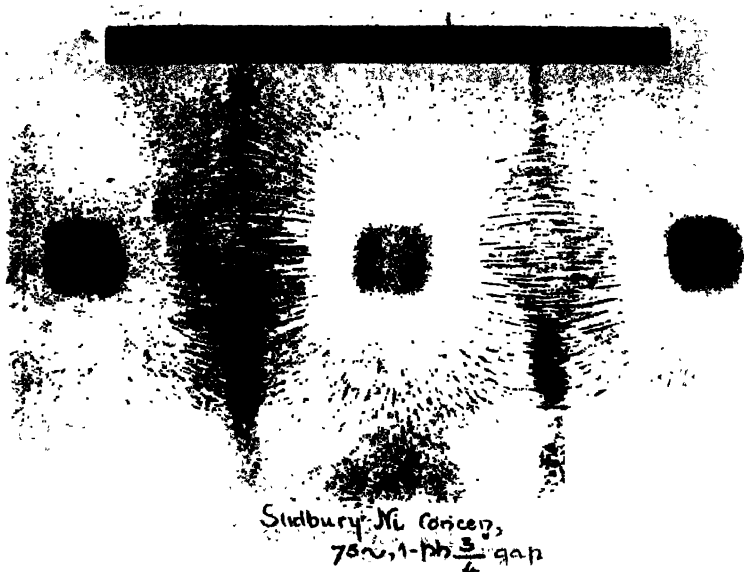


FIG. 7.—SUDBURY ORE OVER A STRONG MULTIPOLAR MAGNET, 1-PHASE.

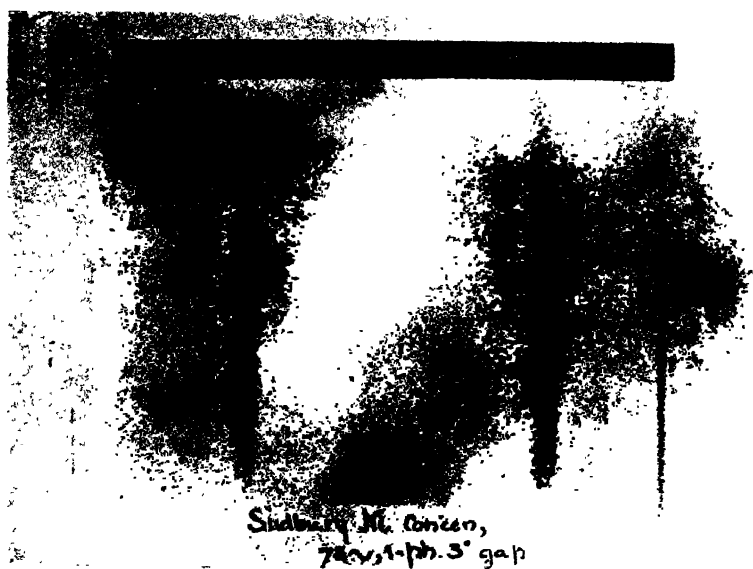


FIG. 8.—SUDBURY ORE OVER A WEAK MULTIPOLAR MAGNET, 1-PHASE.

repulsion. It appears that both attraction and repulsion are always present, and that changes in the field may cause one or other to predominate, attraction however being very weak with this material.

Let us take another example. Over a long narrow multipolar magnet, of which only alternate poles are excited—the purpose of this construction will appear later—specular hæmatite is sprinkled, and the formations shown by Fig. 6 obtained. The halos surround the excited poles. The upper row shows the effect with an air-gap of $\frac{5}{8}$ inch, the lower row with a gap of $\frac{1}{4}$ inch. In the former there is hardly any polar attraction. In the latter much more material is attracted to the poles, and the “equatorial” lines are split by the stray field of the unexcited poles.

As more hæmatite was used for the lower row the density was greater—this should be allowed for in any comparison.

This dual action in one-phase fields is found to be strongly developed in the mineral pyrrhotite, or magnetic pyrites, Fe_7S_8 , and in chalcopyrite, CuFeS_2 , important constituents of the sulphidic nickel ore from Sudbury, Ontario, as is illustrated in Figs. 7 and 8. Over a multipolar one-phase magnet with an air-gap of $\frac{3}{4}$ inch the lines formed by a concentrate of this ore are almost entirely magnetic in character. But on increasing the air-gap to 3 inches, making no other change, the particles rearrange themselves, attraction ceases or is overcome, and the formation changes to the very distinct “equatorial” lines, indicating repulsion, both attraction and repulsion being stronger than with specular hæmatite. Farthest from the poles in Fig. 7—therefore where the field is weakest—there is a distinct formation of “equatorial” lines.

Over one pole of a simple alternate-current bar magnet, both the radial and halo formations may be easily observed, as in Fig. 9.

Slight indications of a dual action appear in some other cases, e.g. in Figs. 2 and 3, where, although the general formations are “axial” there are also “equatorial” indications.

This dual effect does not take place in a one-phase field with iron, nickel, or magnetite, however much the field is altered.

Multiphase Magnets.—So far we have used laminated electromagnets, excited by a one-phase alternating current usually at about fifty periods a second.

Let us now try a long narrow multiphase magnet consisting of a series of upward-pointing poles, the alternate poles being excited by one phase, and the intervening alternate poles by the other phase, of a two-phase supply. This magnet is the same as was used for Fig. 6. It is about 2 feet long, and the poles are 2 inches wide.

It will be understood that in the space above the magnet, when magnetised by multiphase currents, waves of alternating magnetism will sweep along continuously from one end to the other, the direction depending on the relation of the phases, and the speed on the pitch of the poles and the frequency. The speed of these waves at

50 periods a second is nearly 60 feet a second in this case. Resting on this magnet we place a plate of white glass, and on this sprinkle a little of the material to be tried. Let us begin with specular hæmatite. When the current is switched on one phase, halos are formed round the excited poles, as in Fig. 6. When the other phase is switched on, the halos at once begin to move forward along the magnet, breaking up at the same time, the material being repelled laterally from the magnet and deposited in two parallel rows right and left and in a half circle round the end of the magnet. This action is made up of repulsion from the poles, as in the one-phase illustrations Figs. 4, 5, and 6, with the addition of a forward longitudinal propulsion corresponding in direction with the phasal movement; and lateral repulsion to right and left; the final result being that the region over, and for a considerable distance to each side of the line of poles, where the field is strong, is swept clear of the hæmatite, which comes to rest in the regions where the field is weak.

Instead of sprinkling specular hæmatite over the glass plate we will place over one end of the magnet a heap of ore containing that material, as in Fig. 10. On closing the circuit of both phases the hæmatite is driven out of the heap longitudinally and laterally, and deposited in the feebly magnetic regions along the sides and round one end of the magnet, the inert gangue being unmoved. The grey appearance of the concentrate in the figure is caused by reflection from the sparkling or "specular" black crystals. That, in addition to the longitudinal and lateral repulsion, a vertical repulsion is also exerted by the magnet is evident from the fact that particles of the hæmatite are seen to emerge on the surface of the heap, being repelled upward. They are then driven forward longitudinally and laterally, as already described. If a ridge of sand is placed across the plate they climb over it and proceed on their course. The movement of the hæmatite, although slow—it is only a few inches a second—is steady and continuous, being the same whether passing over or near the poles, or between them.

It will be observed that there is strong repulsion of this material by the two-phase magnet, as by the one-phase magnet.

With iron, nickel and magnetite, as already mentioned, ordinary magnetic lines were always formed with one-phase, whether the field was strong or weak—there was no "dual effect," no evident changing from attraction to repulsion on weakening the field.

Let us now go a stage further and try some of these strongly magnetic substances in multiphase fields.

Over one end of the magnet we place a small heap of cast-iron filings. On switching the current on one phase, the filings will be magnetised and will stand up in a bristling heap over the nearest pole. On switching on the other phase the filings will travel slowly and gradually along over the row of poles, showing a strong tendency



FIG 9—SUDBURY ORE OVER ONE POLE OF AN ALTERNATE CURRENT BAR MAGNET, 1 PHASE



FIG 10—SEPARATION OF SPECULAR H₂ MATITE FROM ITS ORE BY A LONG NARROW MULTIPHASE MAGNET

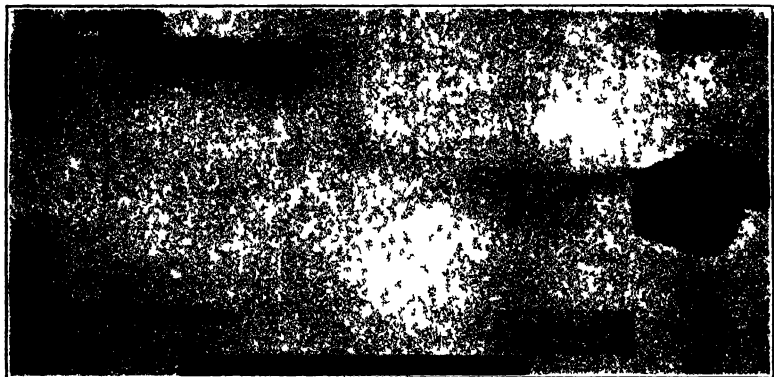


FIG 11 —REPUSSION OF CAST IRON FLINGS BY A MULTIPHASE MAGNET.

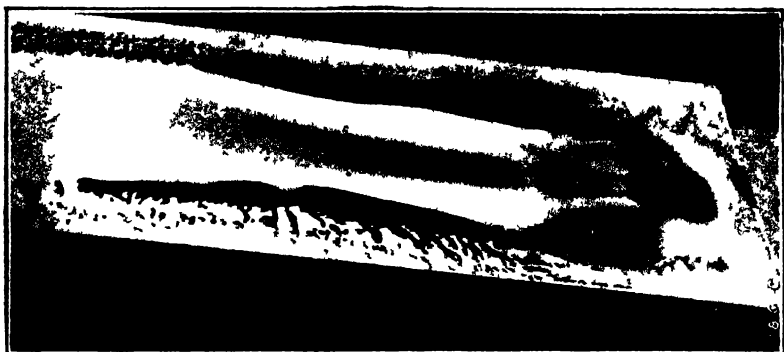


FIG 12 —REPUSSION OF MAGNETITE BY A MULTIPHASE MAGNET

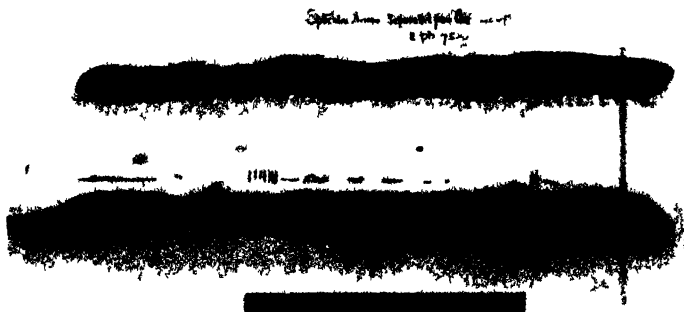


FIG 13 —SEPARATION OF SPECULAR HEMATITE FROM ITS ORE BY A SHORT BROAD MULTIPHASE MAGNET

to stay in adherent tufts over the successive poles, the slowly moving stream being as wide as the poles, and no wider. There is thus a strong magnetic attraction accompanied by a slow longitudinal movement of the particles, which in time will all collect at the other end of the magnet, where they will stand erect. If the current in one phase is reversed the particles will travel back to their original position, in a narrow stream as before.

If instead of resting the glass plate horizontally on the poles of the magnet, we raise one end of it a few inches so as to have a gradually increasing air-gap between it and the magnet, and therefore a gradually decreasing strength of field, and place the heap of filings at the lower end, we find on switching on the two-phase current that the filings begin, as before, to move in a narrow stream over the magnet, but quickly spread out fan-wise, being repelled right and left from the neighbourhood of the magnet, coming to rest beyond the far end of the magnet in the form of a wide horseshoe. Fig. 11 shows this effect. The air-gap between the surface of the poles and the surface of the plate is $\frac{1}{4}$ inch at one end, and 3 inches at the other. The iron filings, therefore, have been propelled longitudinally, and repelled laterally, moving a considerable distance from a strong to a very weak field, and up a considerable incline. Thus, with this very magnetic metal, in a strong field there is longitudinal movement and attraction to the poles; in a weak field there is longitudinal movement and repulsion from the poles, the repulsion increasing as the field is weakened. Unlike the hematite, the iron filings travelled a long way before coming to rest.

The action with magnetite is very similar, as shown in Fig. 12, but in this case the glass plate was horizontal, and at a uniform distance of about 2 inches above the magnet, the lateral repulsion starting at the heap of the material. If the plate rests on the poles, the magnetite, like the iron filings, will travel in a narrow stream over the poles, and will not be repelled laterally. There is a steady and continuous uniformity of motion with the cast iron and other magnetic substances when the field is not strong enough to cause tufting over the poles—that is to say, when the conditions are such that repulsion overcomes attraction.

Stalloy, the highly magnetic low hysteresis iron-silicon alloy—for which the electrical industry has to thank Sir Robert Hadfield and Sir William Barrett—and nickel, show very little tendency to movement, either longitudinal or lateral. They are strongly attracted, repulsion is slight, and is but little increased with distance from the poles.

Fig. 13 shows the action over a multiphase magnet, which instead of being long and narrow was short in the direction of the phase movement, and long—or broad—in the other direction. It consisted of a small number of long parallel poles, the phase movement being at

right angles to the length of the poles. A long heap of specular hæmatite ore was placed at one side of this broad magnet--the upper side in the figure : on switching the current on the hæmatite travelled across the poles and came to rest on the other side of the magnet, in one long continuous heap, leaving the inert gangue behind it. This example differs from the others in one respect. From any point the field is equally strong in both lateral directions--therefore there is no lateral repulsion, and the material is driven straight across the magnet.

All these experiments, for convenience, have been made with dry finely divided materials, but the effects take place even more freely in water, as the materials being then partly in suspension are freer and more mobile.

In the concentration of minerals it is a great advantage to be able to use wet methods. Those who are concerned with such matters may therefore be interested in an effect illustrated by Fig. 14, which may be described as water flowing up-hill. A tall glass test measure containing pulverised Sudbury nickel ore and water is placed in an inclined position over a multiphase electro-magnet. On exciting the magnet the susceptible parts of the ore--mostly pyrrhotite in this case--are repelled or propelled forward and upward, carrying the water with them, the mixture being ejected from the glass vessel and falling into a dish placed to receive it, the inert material remaining in the glass. Although the field was not strong less than 3000 B at the polar surfaces--this repulsion was exerted through a considerable air-gap.

It will be understood that the upward flow of the water is an effect of viscosity, skin-friction, or surface-tension, and that water alone would not move. Minerals vary very much in their behaviour under such conditions.

The dual effect already described with Sudbury nickel ore in a one-phase field has its counterpart in a two-phase field, but the mode of action is different, as illustrated by Fig. 15. A small heap of the ore (A) was placed on a glass plate over a short broad two-phase magnet, the same as used for Fig. 13, the poles and spaces of which are indicated by dotted lines. When the current was switched on, the susceptible material from A was driven across the magnet, some of it being deposited at B where the magnet ended, the remainder being repelled beyond the magnet to C. These two quite distinct deposits were found on chemical and microscopic examination to be almost alike--both being mainly pyrrhotite--the difference in action being therefore due to physical causes, not to difference of composition. The inert material remained at A. It is suggested that, as the action was rather violent, some of the material was projected slightly beyond the magnet, thus, getting into a weaker field, it was repelled still further, forming the portion "C." The fan-shaped appearance of "C" is consistent with this suggestion.

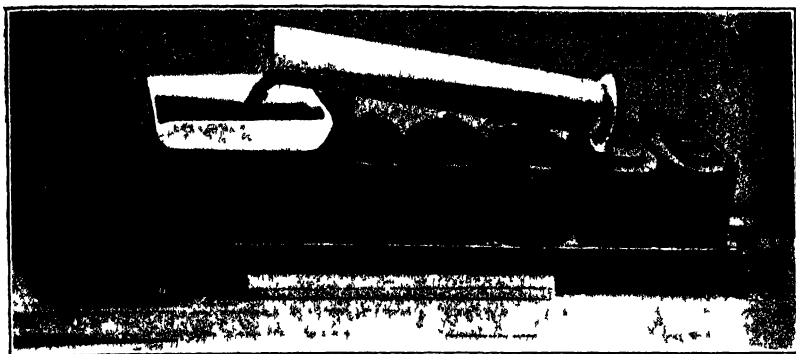


FIG 14 ' WATER FLOWING UP HILL

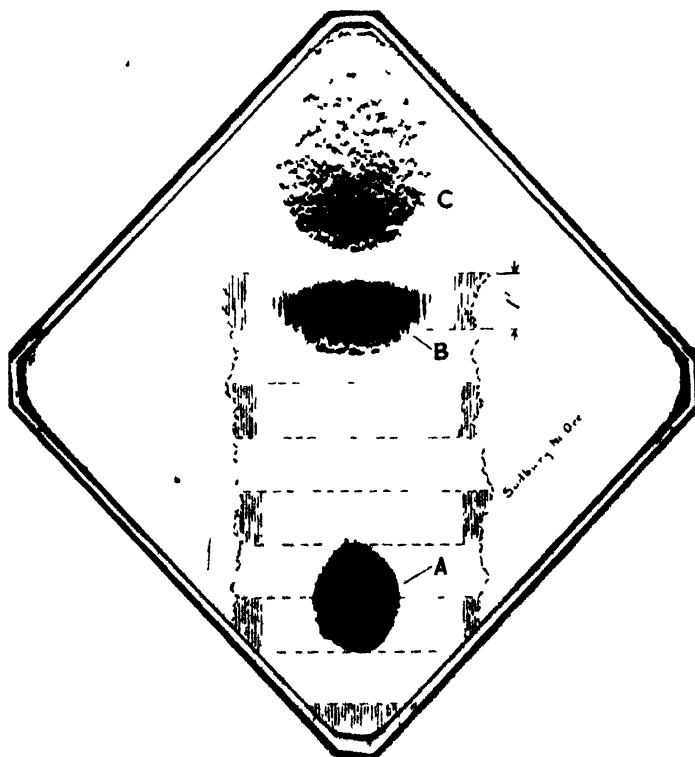


FIG 15 —“DUAL EFFECT” WITH SUDBURY ORE OVER A MULTIPHASE MAGNET.

Bismuth.—It should be noted very particularly that bismuth, the most dia-magnetic substance known, is inert and motionless in an alternating magnetic field whether one-phase or multiphase.

Effect of Distance.—It is well known that with uni-directional magnets attraction decreases very rapidly as the distance from the poles increases. For example, a magnet which supported 5 lb. with the keeper in contact with the poles, supported less than $\frac{1}{2}$ lb. at a distance of $\frac{1}{4}$ inch.

The curve, Fig. 16, obtained with a two-phase magnet, shows that so far as movement can be used for comparison the effect is entirely different. The ordinates represent the reciprocal of the time in seconds, i.e. the speed at which the magnet repelled the particles ;

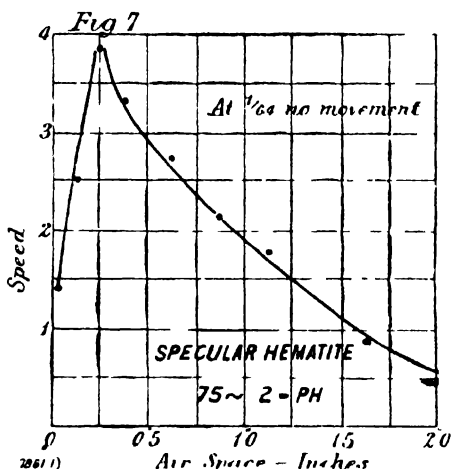


FIG. 16.—CURVE ILLUSTRATING VARIATION OF MOVEMENT WITH DISTANCE FROM POLES.

the abscissæ mark the air-gap in inches. There was no movement at $\frac{1}{4}$ inch very close to the poles. At $\frac{1}{2}$ inch the speed was 1.5, at $\frac{1}{4}$ inch it was 4, then gradually fell off again, but at a much slower rate than the attraction with a uni-directional magnet. As it does not seem possible that the change in speed can be due to a corresponding change in the induction at the various distances, some other explanation must be sought. It is perhaps possible that as the induction falls off it may be counterbalanced by an increase in what, for lack of a better term, may be called the interlacing or meshing of the phases.

The curve is from tests with a small magnet. With larger magnets much greater values are obtained, but the general character of the curves is unaltered.

Planes of Force.—Another effect may now be described. Some finely divided magnetic substances when placed over a strong multi-phase magnet form high planes, laminae, or fins extending lengthwise over a row of poles, their distance apart being several millimetres, increasing with the strength of the field. They may move forward slowly and irregularly, but with some substances they remain stationary. These planes are evidently mutually repellent. Over a wide magnet they stand upright, parallel with one another. Along the centre line of the poles of a narrow magnet they are vertical. Towards the sides of the magnet they lean over in accord with the disposition of the field and the unbalanced mutual repulsion, becoming almost horizontal. They have considerable rigidity although they are very thin; with very finely powdered material they seem to be only the thickness of single particles, and are partly transparent. If the dish containing them is moved to and fro sideways they sway sideways flexibly, doubtless in an effort to keep in line with the magnetic flux. Although standing over and in line with the laminae of the magnet core, there is no numerical relation between them, as is shown by their distance apart increasing with the field. They grow in height by upward vertical repulsion of the particles, their upper portions becoming unsteady when the limit of height is reached, indicating that at that height the force of repulsion has overcome that of attraction and gravitation. When that occurs the upper particles often travel along the tops of the planes by a rotating motion. Their height may reach $1\frac{1}{2}$ or 2 inches.

On weakening the field or raising the dish these planes break up, the material moving forward, gradually scattering to right and left, if the magnet is narrow.

Fig. 17 shows the planes of force formed by powdered loadstone. Some of this material was placed in a photographic dish 2 inches deep, resting on the poles of a wide two-phase magnet. On switching the current on, the material at once began to form planes, being at the same time driven to the end of the dish, where further propulsion being prevented the planes increased in height and remained slightly trembling, but otherwise without motion. The whole process of building up occupies only one or two minutes. The upper portions of the planes on reaching the top of the dish were driven over it and dissipated. If the current is kept on for more than a few minutes the planes get slightly warm to the touch, doubtless from hysteresis.

The rigidity of the planes is considerable. If pressed down by the finger they break, but quickly build up again when the pressure is removed. So rigid are they that when the current is switched off the planes often remain standing. Fig. 18 shows planes of magnetite remaining standing after the current has been cut off.

An attempt may be made to explain the planes of force—if that term may be allowed. They are quite different from the lines of force in the field of a magnet or the tufts which form over or

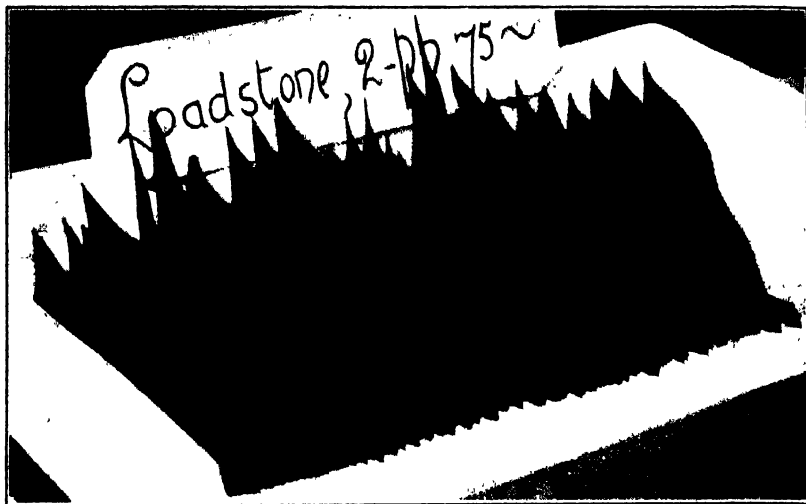


FIG. 17.—PLANES OF FORCE FORMED BY POWDERED LOADSTONE IN A MULTIPHASE FIELD.

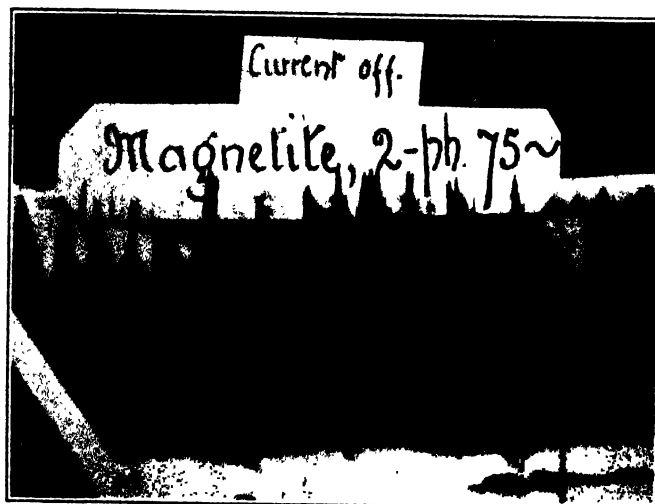


FIG. 18.—PLANES OF FORCE FORMED BY MAGNETITE REMAINING STANDING AFTER THE CURRENT WAS SWITCHED OFF.

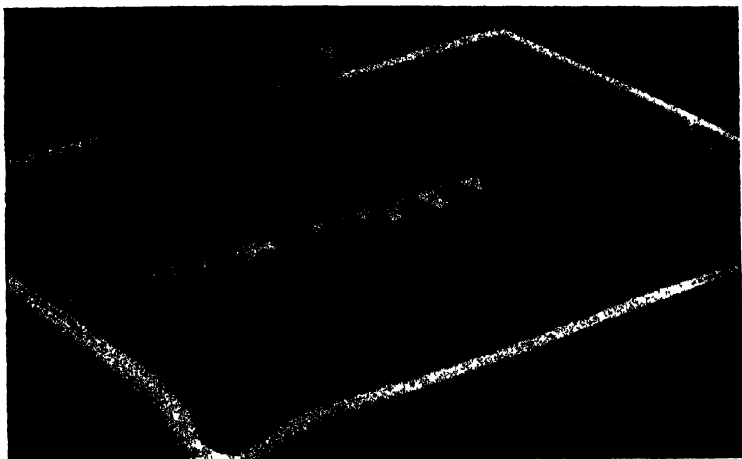


FIG. 19.—IMPERFECT PLANES OF FORCE FORMED BY NICKEL OVER
SHORT BROAD MAGNET.

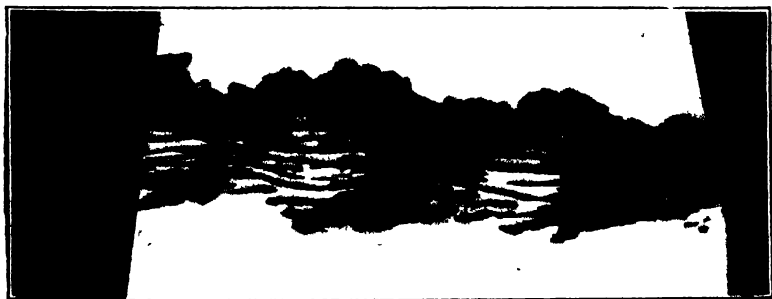


FIG. 20.—IMPERFECT PLANES OF FORCE FORMED BY STALLO OVER
NARROW MAGNET.

near the poles of a magnet whether uni-directional or one-phase. They are caused by the forward propelling action of the moving multiphase field, and are built up by the upward repulsion exerted by that field, and are forced apart by mutual repulsion. These planes of force are traversed by what for convenience may be termed alternating magnetic currents. Through the successive changes of this rapidly moving magnetism, all parts facing one another on the sides of adjacent planes are magnetically equi-potential, and therefore mutually repellent, the lateral repulsion separating, compressing, and flattening the planes, and giving them rigidity.

Hard steel or cast-iron filings, cobalt and ordinary magnetite form planes of force very much the same as the loadstone in the figure.

Stalloy and nickel, however, behave very differently. They do not move along to the end of the dish, and form only small and irregular planes. For example, Fig. 19 shows the result with nickel under precisely similar conditions to those used for Fig. 17.

Over a long narrow magnet the formation assumed by stalloy is seen in Fig. 20. The inclined positions of the materials towards the sides of the magnet will be noticed.

Suggested Explanations.—The remainder of our time must be devoted to a consideration of the possible causes of the effects put before you.

In one-phase and in multiphase fields the effects differ in some ways, but in all cases two opposed forces appear to be concerned, attraction and repulsion, which vary in different ratios with variations in the strength of the field, and in actual and relative values in different materials. With some materials they are so nearly balanced that a comparatively small change in the field causes one or the other to become predominant – attraction overcoming repulsion, or the reverse. With other materials it is suggested that the difference is so great that such a conversion cannot be brought about, except possibly by field variations greater than we have tried.

The explanation of attraction by alternate-current magnets presents no difficulty. The difficulty is to account for the repulsion, which, even if not predominant, is assumed to be always present.

Two possible causes will occur to all – that it may be due to eddy-current repulsion or to dia-magnetic repulsion. The first is unlikely, as eddy currents must be very small indeed in materials of very high specific resistance, such as some of those we have used, especially when finely divided. On putting powdered aluminium in the alternate-current field, whether one-phase or multiphase, there is no movement. As aluminium has a very low specific resistance, the eddies in it under similar conditions of field and sub-division must, relatively, be very large, and therefore this absence of movement in aluminium appears to justify us in concluding that eddy currents cannot be the cause of the repulsion of the other materials.

On examination dia-magnetic repulsion fails to provide an

explanation. Faraday defined a dia-magnetic substance as one that took up a position between the poles of a magnet at right angles to the ordinary magnetic lines of force; this he termed the "equatorial" position. Magnetic substances were those that took up a position joining the poles—this he termed the "axial" position. This defined but did not explain. Faraday added an explanation, showing that the determining factor was the environment—magnetic substances were those that were more magnetic than air, dia-magnetic substances were those that were less magnetic than air.*

But we must remember that Faraday's researches on dia-magnetism were carried out with uni-directional magnets, and his definitions had reference to that. All the substances used in our experiments are magnetic by these definitions and by ordinary tests.† But in alternating current fields another set of conditions is encountered—there is this phenomenon of dual action—substances which are magnetic in a uni-directional field or in a strong alternate-current field, act in a weak alternate-current field as if they were dia-magnetic—much more strongly dia-magnetic than bismuth or any other admittedly dia-magnetic substances—for the "equatorial" lines in some of our figures are far more strongly defined than any that could be produced by any known dia-magnetic materials in uni-directional fields.

It is contended that we are not dealing with true dia-magnetism in such cases, but that the magnetic state of the material is or may be overcome by an anti-magnetic force set up by the alternating field.

The conclusion seems unavoidable that we must look elsewhere than to eddy current repulsion or to dia-magnetic repulsion, as ordinarily understood, for an explanation of this phenomenon.

The problem may be re-stated thus: All the materials used—and probably all magnetic materials—appear to develop both attraction and repulsion in alternating magnetic fields, these opposing forces varying in different materials in amount and in their relation to one another. These forces appear to be differently affected by changes in the field, in all cases attraction decreasing more rapidly than repulsion as the field is weakened.

* Exp. Res. Vol. iii, p. 30, No. 2252; p. 71, No. 2424, Dec. 1845.

† Some explanation is called for as to specular hematite. It generally occurs in nature associated with a little magnetite—for that reason its magnetic properties are apt to be over-rated. If finely crushed some magnetite may generally be removed from it, even by a permanent magnet. The residue will then be found to be quite inert when sprinkled on a glass plate over a strong uni-directional electro-magnet, the friction being enough to prevent movement. A simple but very delicate test is to sprinkle a little of it on water in a shallow dish. It will float, and if a weak permanent magnet be placed under the dish, the particles will slowly collect in an unorganised group and float over the poles, showing that it is very feebly magnetic. Tested by Faraday's method of suspension in a glass tube between the poles of a magnet it assumes the "axial" position.

What known properties of magnetic substances accord with these effects ?

As already pointed out the attraction presents no great difficulty. It is more or less the same as with uni-directional magnetism, falling off rapidly—at least as rapidly as the square of the induction.

Of the known properties of magnetic substances there remains one to consider—magnetic hysteresis, the tendency of changes of magnetism to lag behind the magnetising force, causing a dissipation of energy.*

Although it has never been associated with repulsion the lecturer has always attributed these various repulsion effects to hysteresis, for the simple reason that he has found them greatest in substances in which the hysteresis was large and least in those in which it was small.

In one important respect hysteresis complies with a condition necessary to the solution of our problem : —

Whereas magnetic attraction falls off at least as the square of the induction, hysteresis usually decreases only as $B^{1/2}$.

The hysteresis co-efficients of some of those substances are as follows :—

—	Hysteresis Coefficient	From tests by
Stalloy	0 00076	The Author
Nickel	0 001 to 0 0012	Kennelly
Cobalt	0 012	Steinmetz
Grey Cast Iron	0 013	"
Magnetite	0 0235	"
Hardened Steel	0 025	"
Specular Hæmatite	See below	T. Townsend Smith

These values are based on tests of pieces of considerable size. As filing or crushing will almost certainly greatly increase the hysteresis, the table can only be considered as a guide to the relative properties of the finely divided materials.

Stalloy, which shows the least repulsion of all, stands at the head of the list with the least hysteresis ; next comes nickel, which is almost as free from repulsion as stalloy.

The next four substances in the list are strongly magnetic, have high hysteresis co-efficients—15 to 30 times as high as stalloy—and under suitable conditions are all strongly repelled from multiphase magnets.

The very low permeability of specular hæmatite has made it difficult to understand its repulsion except on the assumption that its

hysteresis was very great. A paper by T. Townsend Smith * removes this difficulty. The hysteresis is enormous, but its value cannot conveniently be expressed as a co-efficient. An example will however suffice.

The hysteresis loss in stalloy at an induction of 91·3 B was found by Wild † to be 0·27 ergs per cycle.

Townsend Smith gives the hysteresis loss in specular hæmatite, at the same induction, as 144 ergs per cycle, or 535 times as great as in stalloy.

Clearly there is a very close relation between repulsion and hysteresis. This leads to the supposition that there may be an analogy between the action we are considering and the action of conductors in an alternating field.

Lenz's law for the latter is to the effect that the induced currents in a conductor are always such as to oppose the motion producing them, and therefore to cause the conductor to retreat from the inducing field. It was thought that possibly the magnetic reaction in a hysteretic substance might be such as to oppose the field producing the hysteresis—and therefore to cause the substance to retreat from that field. But as none of the authorities consulted will admit the soundness of such an analogy—or even that the repulsion can be caused by hysteresis, although most of them say they do not know what else it can be—the lecturer must perforce cease to call the effect “hysteretic repulsion,” and be content for the present to regard it as an effect associated with hysteresis!

The Lecturer wishes to express his thanks to the Governing Body of the Imperial College of Science and Technology for kindly permitting him to pursue this matter in the Laboratories of the Royal School of Mines and the City and Guilds Engineering College—and to Professors Truscott and Fortescue for facilitating that work.

He also wishes to refer to his indebtedness to the late Sir James Dewar, one of whose last official acts before his illness was to do him the honour of inviting him to give this Discourse.

[W. M. M.]

* T. Townsend Smith, “Magnetization and Hysteresis in Hematite Crystals,” *Physical Review* (U.S.A.), vol. xv, p. 345, May 1920.

† L. W. Wild, “The Magnetisation of Iron at Low Inductions,” *Journ. I.E.E.*, vol. 52, p. 96, 1913.

Friday, June 1, 1923.

THE RIGHT HON. LORD ROTHSCHILD, F.R.S.,
Vice-President, in the Chair.

PROF. HENDRIK ANTOON LORENTZ, Hon. F.R.S., Hon. M.R.I.,
Ph.D., Leiden University.

The Radiation of Light.

BEFORE beginning my lecture I want to say in the first place that I feel it as a great honour to have been invited by this Institution that has been made famous all over the world by the scientific men who worked in it, and in which, above all, there is so much that reminds us of Michael Faraday, the greatest discoverer in physical science perhaps who ever lived. Allow me in the second place to pay a tribute to the memory of Sir James Dewar, whose loss all physicists deeply deplore, thinking with great admiration of the talent with which he opened new paths of research. He has worthily continued the history of the Royal Institution, which forms an important chapter in the history of science itself.

One of the lessons which this history of science teaches us is surely this, that we must not too soon be satisfied with what we have achieved. The way of scientific progress is not a straight one which we can steadfastly pursue. We are continually seeking our course, now trying one path and then another, many times groping in the dark, and sometimes even retracing our steps. So it may happen that ideas which we thought could be abandoned once for all, have again to be taken up and come to new life.

These remarks are well illustrated by the way in which at different times physicists have represented to themselves the way in which light is produced and radiated. You all know the two contending views, the emission theory or the corpuscular theory of light, developed by Newton, and the undulatory theory proposed by Huygens, perfected afterwards by Young and Fresnel, and newly shaped as the electromagnetic theory of light by Clerk Maxwell. I should now like to point out to you how these two theories, however widely different their principles may be, were interwoven in Newton's mind, and how it is well possible that they will be interwoven again in the physics of the future.

When one reads Newton's Optics, one cannot doubt that, when

he speaks of a ray of light, he always thinks of a stream of small corpuscles emitted by a luminous body and moving along in straight lines, so long as they are not acted upon by some deflecting force. The phenomenon of diffraction, as we call it now, that had been discovered by Grimaldi and which Newton carefully examined experimentally, I mean the phenomenon that the shadow of a thin wire, for instance, is wider than it would be in the case of undisturbed rectilinear propagation, was attributed by Newton to certain repulsive forces with which the wire acts upon the rays of light when they pass along its surface at a very small distance.

The reflection and the refraction of light were likewise considered as due to forces which act upon the corpuscles of a ray when they come near the surface of separation of two media, like air and glass or water. Newton expressly states that the corpuscles must not be conceived to be reflected by the *individual* molecules of the body on which they impinge. If we could see the molecules, we should find the surface to be very rough, and it would be clear that their individual actions can hardly lead to a regular specular reflection. For this reason Newton supposes that the corpuscles of light are acted upon, not by the molecules separately, but by parts of the bodies containing a great number of them. This does not prevent us from supposing the actions in question to be appreciable at very small distances only. If they were sensible up to one ten-thousandth of a millimetre, for instance, and if you had a corpuscle situated at half that distance from a polished plate of glass, then, since the structure of the glass is very fine grained with respect to the distance in question, the corpuscle would be acted upon by an immense number of molecules, and the discontinuities would not make themselves felt, so that it would be as if we had a perfectly smooth surface.

The forces of which I am speaking are comparable to those that were introduced much later by Laplace in the theory of capillarity. A corpuscle in the interior of a body will experience equal forces in all directions, so that there will be no resulting force and the particle continues its way with a constant velocity. It is only in a very thin layer extending on both sides of the surface of separation, that there will be a resulting force, due to the unequal attractions, or perhaps repulsions, which the two media exert on the corpuscle. For reasons of symmetry the resulting force is perpendicular to the surface of separation, and therefore, whether the corpuscle be reflected into the first medium or allowed to continue its way in the second, the component of the velocity in the direction of the surface will remain unchanged. From this you can easily deduce the law of reflection. As to that of refraction, a simple diagram (Fig. 1) shows that, if the velocity along the surface AB is the same before and after the refraction, the sines of the angles which the ray makes with the normal NN, the angle of incidence i and the angle of refraction r ,

will be inversely proportional to the velocities, say v_1 and v_2 , with which the corpuscles move on the two sides of the surface; indeed, since the component of the velocity along the surface is $v_1 \sin i$ on one side, and $v_2 \sin r$ on the other, its constancy requires that

$$\sin i : \sin r = v_2 : v_1.$$

We shall therefore have found the well-known law of refraction, viz. the constancy of the ratio between the two sines, if we suppose v_1 and v_2 to have definite values, whatever be the angle of incidence. Now, if the first medium is air, or rather the ether, we shall suppose v_1 to have a definite value, at least for rays of a particular colour, on account of the way in which light is emitted. Once taking for

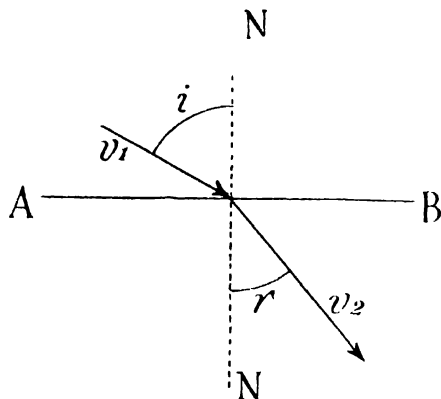


FIG. 1.

granted this constancy of v_1 , we can assure ourselves of that of v_2 by taking into account that the passage of a corpuscle from the interior of the first medium to the interior of the second will be accompanied by a definite change in the value of the potential energy, this value being in each medium the same for all positions of the corpuscle and whatever be its motion. By the law of conservation of energy the change in the kinetic energy of the corpuscle must be equal and opposite to that of the potential energy; thus, the difference $v_1^2 - v_2^2$ must be the same in all cases, and the constancy of v_2 follows from that of v_1 .

I shall dwell no longer upon the further development of the corpuscular theory, but I must now point out to you how Newton also had the notion of vibrations, and even of waves, that are propagated in a medium. He was led to this by his experiments on the colours of thin plates, which we now attribute to interference, and

which he examined very carefully for the case of the thin layer of air contained between a plane surface of glass and a surface that is slightly convex. Here we have the phenomenon generally known as Newton's rings. Suppose the light to be homogeneous and the incidence to be normal. Then, both in the reflected and in the transmitted light, you will see a number of alternating bright and dark rings, the dark rings in the transmitted light having the same diameters as the bright ones in the reflected light. This means of course, what is quite natural, that, at a thickness of the layer for which a great part of the light is reflected, only a small part is transmitted, and conversely.

The experiment shows that, of all the rays that enter at the front surface of the layer, some will be reflected at the back surface and others not, and that this depends on the thickness of the layer, the distance between the two surfaces. Further, that there is a certain periodicity in this. Now, since two rays, one of which is reflected at the back surface and the other not, must obviously be more or less different, Newton supposes that, after having passed the first surface, a ray or a corpuscle is in alternating states, *fits*, as he calls them, *of easy reflection and easy transmission*. But I think I had better give you this in his own words : —

“ What kind of action or disposition this is ; whether it consists in a circulating or a vibrating motion of the Ray, or of the Medium, or something else, I do not here enquire. Those that are averse from assenting to any new Discoveries, but such as they can explain by an Hypothesis, may for the present suppose, that as Stones by falling upon Water put the Water into an undulating Motion, and all Bodies by percussion excite vibrations in the Air ; so the Rays of Light, by impinging on any refracting or reflecting Surface, excite vibrations in the refracting or reflecting Medium or Substance, and by exciting them agitate the solid parts, of the refracting or reflecting Body, and by agitating them cause the Body to grow warm or hot : that the vibrations thus excited are propagated in the refracting or reflecting Medium or Substance, much after the manner that vibrations are propagated in the Air for causing Sound, and move faster than the Rays so as to overtake them ; and that when any Ray is in that part of the vibration which conspires with its Motion, it easily breaks through a refracting Surface, but when it is in the contrary part of the vibration which impedes its Motion, it is easily reflected ; and, by consequence, that every Ray is successively disposed to be easily reflected, or easily transmitted, by every vibration which overtakes it. But whether this Hypothesis be true or false I do not here consider. I content my self with the bare Discovery, that the Rays of Light are by some cause or other alternately disposed to be reflected or refracted for many vicissitudes.”

Let me add that, in order to account for the fact that light falling on a surface of glass is partially reflected and partially transmitted,

Newton assumed that fits of easy transmission and easy reflection exist already in the incident rays before they reach the surface. He supposed *these* fits to have been impressed on the rays already in the act of emission itself; in fact he went so far as to imagine something like vibrations to go on in the source of light. Query VIII near the end of the book begins with the words:—

“Do not all fix’d Bodies, when heated beyond a certain degree, emit Light and shine; and is not this Emission perform’d by the vibrating motions of their parts?”

So there was much of vibratory or undulatory theory in Newton’s ideas, though he seems never to have thought, as Huygens did, of the ray itself consisting in a propagation of waves. In Query XVII he again compares the ray of light falling on the surface of some substance to a stone thrown into stagnant water.

As you all know, the conclusion that the sines of the angles of incidence and refraction would be *inversely* proportional to the velocities of propagation became fatal to the corpuscular theory. The undulatory theory required that the two sines be *directly* proportional to the velocities of propagation, and when, about a century ago, the velocity of light in water could be measured, the result was in full agreement with the wave theory. I can briefly state the facts by saying that the index of refraction of water is about $4/3$. The velocity of light in water ought therefore to be $3/4$ of that in air according to the undulatory theory, and so it was found to be, but the corpuscular theory requires that it should be greater than the velocity in air, viz. $4/3$ times that velocity.

There now came a period during which the wave theory reigned supreme, until in these last ten or twenty years physicists were led to ideas, not exactly the same as Newton’s, but still more or less similar to the notions of the corpuscular theory.

The beginning of it was that, on the basis of the electromagnetic theory, a beam of light was recognized to possess a certain momentum, comparable to that of a moving ball. For the ball the momentum is given by the product $m v$ of the mass and the velocity, and when we attribute to the beam of light a certain momentum, say an amount Q of it, we simply mean to say that the beam has the same power of setting bodies in motion as a body would have, for which the product $m v$ has just that value Q .

The existence of momentum in a beam of light is shown by the pressure of radiation that was predicted by Clerk Maxwell, and observed and measured first by Lebedew and afterwards by E. F. Nichols and Hull. Let us consider this question for the case of a beam of light falling normally on a perfectly reflecting mirror, and let us compare the explanation by the undulatory theory, and the explanation that could be given by a follower of Newton, if there were one in these times. For the sake of simplicity I shall suppose that we hold the mirror in position by applying to it a certain force.

If we can calculate that force we shall also know the pressure on the mirror, to which it is equal.

In the experiments the pressure has been compared to the energy which, in the beam of light, falls on the mirror in unit of time, the two quantities being proportional to each other. Now, according to both theories, the momentum which falls on the mirror has its direction reversed, and the ratio in question will be equal to that of twice the momentum of the light that reaches the surface during a certain time, to the energy of that same light. In the corpuscular theory this would be the ratio of $2 m v$ to $\frac{1}{2} m v^2$, or $4, v$; thus, when c is the speed of light, $4/c$. On the undulatory theory the ratio between the momentum and the energy of a beam is that of 1 to c , by which the result becomes $2/c$. You see that, for a beam of a given intensity, the pressure would be different in the two theories, in the undulatory theory half only of what it would be on the other view, so that here again we have a crucial experiment. The measurements have clearly decided in favour of the wave theory.

Our neo-Newtonian would have to own himself defeated by this, if he had been taught classical mechanics only, and had never heard of the changes that have been brought about by the theory of relativity. If he has studied this latter theory there is an escape for him; indeed, he can point out triumphantly that the values which relativity assigns to the momentum and the energy of any moving system are such that our last result $2/c$ holds in all cases. Only, this appeal to relativity would imply that the corpuscles become widely different from what they were originally thought to be. According to relativity dynamics a thing moving with the speed of light and having a finite mass, however small it may be, would have an infinite momentum and an infinite energy. Therefore, since the pressure has a finite magnitude, a corpuscle must be something with no mass m at all, but which, nevertheless, when moving with the velocity c , has a finite energy and momentum. By these assumptions the corpuscles become much like the so-called light quanta of modern theory, about which I should now like to say some words.

The word "quanta" is used by physicists in two different senses. In some cases we mean by it no more than definite amounts of energy of radiation, whose magnitude is proportional to the frequency ν , or number of vibrations in unit of time, so that it can be represented by $h\nu$, where h is a constant. In this form the idea originated with Planck, who used it in the problems of heat radiation, and after whom the constant h is generally called. In Bohr's theory of spectral lines these minute amounts of energy play a fundamental and most important part; one of his assumptions being that light is not emitted in quantities of any magnitude, but in a greater or smaller number of full quanta that are radiated successively, one at a time.

It ought to be remarked that in this form the notion of quanta has nothing that is very startling or mysterious. If a tuning fork is

made to vibrate by taps of a definite intensity, the fork being allowed to lose all its energy before it receives a new blow, we shall have emission of "sound quanta." We can imagine without difficulty that similarly in a source of light the energy is measured out in small but finite portions of a fixed magnitude.

However, this does not always suffice. There are phenomena from which, if we had to judge by them solely, we should certainly infer that the energy of a quantum not only has a definite amount, *but also remains confined to a very small space*. In this way one has been led to the idea of "concentrated quanta," which may well be said to be Newton's corpuscles in a modernized form.

The phenomena to which I alluded are those of photo-electricity. When light of a suitable frequency is let fall on a plate of a properly chosen substance, electrons are set free, and it has been found that the energy of each of these electrons is equal to the quantum for the light which we use. This can be easily understood if the quanta are confined to small spaces, so that the electron can catch at once a whole quantum, whereas, when a quantum is spread out over a considerable extent, it is very difficult to see how an electron is to get hold of it. So the phenomena of photo-electricity seem to speak in favour of some corpuscular theory.

Let us, in order to make this clearer, suppose that the sensitive plate is first placed at a small distance from the source of light, and is then removed to a distance a hundred times as great, so that the intensity of the light or the total energy that falls on the plate in a certain time becomes 10,000 times less. Observation shows that the number of electrons liberated from the plate also becomes 10,000 times less, but that they are ejected with exactly the same velocity as before. This would be very natural if we could adopt some form of corpuscular theory, either the old or the modernized one. Then it would be clear that the number of corpuscles striking the plate has diminished in the ratio I mentioned, but that each individual corpuscle can do just what it did at the smaller distance, for the velocity has not been altered, and the corpuscle or the concentrated quantum has lost none of its properties.

On the contrary, when there are no concentrations, when, in spreading out, the energy becomes more and more dilute, we should expect that, at a certain distance, the light becomes too feeble ever to liberate an electron.

So it would seem that we really want concentrated quanta. But now, having recognized this, we have to face a very serious difficulty, a difficulty that hangs as a heavy cloud over this part of physics. Indeed, the existence of narrowly limited disturbances of equilibrium is absolutely irreconcilable with the principles of the undulatory theory as they are embodied, for instance, in Maxwell's equations of the electromagnetic field. According to these equations a disturbance of the state of the ether can never remain confined within a

space of constant magnitude ; around each point that is reached by the disturbance there is a propagation in all directions, and so there is always the tendency to a lateral expansion that becomes manifest in the phenomena of diffraction. It is true that, when our openings are wide in comparison with the wave-length, we may have beams of light that are rather sharply defined over a certain length, but if we go far enough along the beam we shall ultimately notice an unlimited expansion. When, for instance, parallel rays are made to pass through an opening of one centimetre in diameter, we shall observe an illuminated circle of the same magnitude with a rather sharp border on a screen at a distance of some metres, but if the screen is removed to a distance of 100 kilometres, there will be a badly defined patch of light extending over something like half a metre. Or, again, take the case of a disturbance initially confined within a spherical space a centimetre in diameter. At some later instant it will be found in a shell of this thickness, bounded by two concentric spheres which both expand with the speed of light. By properly choosing the distribution of the disturbance in the initial sphere, you have it in your power to produce different distributions in the expanding shell, but you can never prevent the disturbance from ultimately occupying a very considerable part of the spherical wave.

One might object that these are mostly theoretical inferences and that we must never swear by a theory, not even by Maxwell's. Let me therefore conclude by pointing out that, so far as we can see now, the hypothesis of concentrated quanta is directly in contradiction with observed facts, viz. with what is seen in the phenomena of interference.

You know that bright and dark interference fringes can never be produced by means of two different, mutually independent, sources of light ; we explain this by the want of all coherence between the vibrations in one source and those in the other. Now, the elementary acts of emission, in each of which a quantum is radiated, must certainly be incoherent ; they may take place in different atoms, and there is not the least reason why there should be any connection between what goes on in one atom and in another. Hence, when we observe an interference phenomenon, *one* quantum taken by itself must be able to produce it, and this will enable us to draw some conclusions concerning the extension of a quantum in different directions.

In certain experiments made with highly homogeneous light, interference fringes have been observed, produced by rays whose paths differed by more than a million of wave-lengths. This means that there was a regular succession of more than a million of waves, and, since all these waves must be contained in one quantum, the length of a quantum in the direction of propagation must have been more than, say, 50 cm. That the lateral dimensions must be no less considerable is shown by the influence which the aperture of an optical instrument has on the quality of the images, and consequently

on the resolving power. Let L (Fig. 2) be the objective glass of a telescope, a "perfect" lens from the point of view of geometrical optics, so that, if there were no diffraction, the rays R coming from a distant star would converge exactly towards the focus F . In reality this can never be; on the plane V there will be an illuminated spot of a certain extent, and if we want to have this spot small, so that there is a sharply defined image of the star, we must use a large lens. As a matter of fact this is one of the advantages of the great modern telescopes.

Let us conceive the opening of the telescope to be divided into two parts, say of equal areas, a central circle L_1 and a ring L_2 around it. If, by means of a screen with a circular opening, we reduce the

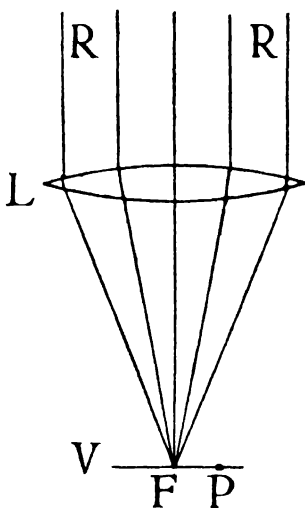


FIG. 2

aperture to the part L_1 , the image of the star becomes less sharp; a point P at a small distance from F , which remains dark when the full aperture is used, may now be illuminated, the light disappearing again when the screen before the lens is removed. The explanation is, of course, that the vibrations which P receives from L_1 are counteracted by opposite ones coming from the part L_2 . So, the fact that a large opening actually has the effect on the quality of the image which we expected from it, shows that there is interference between vibrations reaching the lens at different points of its surface. According to what we saw these vibrations must belong to one and the same quantum, and we may therefore conclude that the lateral extension of a quantum is comparable to the size of the objective.

The remarkable experiments by which Prof. Michelson has been able to measure the diameter of some stars allow us to push the argument still farther. In his apparatus a beam carrying four mirrors, 1, 2, 3, 4, was placed in front of the opening of the telescope, the mirrors 2 and 3 occupying places within the opening, whereas 1 and 4 were outside the opening, on opposite sides of it. The mirrors were adjusted in such a way that two beams of rays coming from the star entered the instrument, the one being reflected by the mirrors 1 and 2, the other by 4 and 3. The fact that under these circumstances interference fringes appear in the field of view proves that a quantum must reach from one of the outer mirrors to the other. The distance between these mirrors was no less than 6 metres.

The discrepancy between these estimates of the size of a quantum, according to which it would be too big to enter our eye, and, on the other hand, the notion that it is small enough to be captured by a single electron, is certainly very wide. Yet the laws of the two classes of phenomena about which we have reasoned, the phenomena of interference and those of photo-electricity, are so well established that there can be no real contradiction between what we deduce from one class and from the other; it must after all be possible to reconcile the different ideas. Here is an important problem for the physics of the next future. We cannot help thinking that the solution will be found in some happy combination of extended waves and concentrated quanta, the waves being made responsible for interference and the quanta for photo-electricity.

[H. A. L.]

Friday, June 15, 1923.

SIR EDWARD POLLOCK, F.R.C.S., Manager and Vice-President,
in the Chair.

SIR ERNEST RUTHERFORD, D.Sc. LL.D. F.R.S.,
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Life History of an Alpha Particle from Radium.

IN this lecture I propose to discuss some of the properties of the high-speed α -particle which is ejected spontaneously from radioactive substances. This flying atomic nucleus is not only the most energetic projectile known to us, but it is also an agent of great power in probing the structure of atoms, so that an account of the effects produced by it is of wide scientific interest.

It is now well established that the α -particle expelled from radioactive bodies is in all cases a helium atom, or, to be more precise, the nucleus of a helium atom of mass 4 carrying two positive charges of electricity. It is only when the expelled nucleus is stopped by its passage through matter that it captures the two negative electrons required to convert it into the neutral helium atom. It is natural to suppose that the helium nucleus, which is shot out at great speed from the heavy nucleus of a radioactive atom, formed part of its structure. For some reason, which is not as yet understood, occasionally one of the radioactive nuclei breaks up with explosive violence, ejecting the component helium nucleus with high velocity. It is probable that the α -particle in escaping from the radioactive nucleus acquires part of its great energy of motion in passing through the repulsive electric field surrounding the latter, but at present we do not know the nature of the forces which hold the complex nucleus together, or whether the α -particle is at rest or in orbital motion in the nuclear structure before instability sets in. We know, however, that there is a very wide range of stability exhibited by different radioactive elements. In a substance like radium A the average life of the radioactive atom before ejection of an α -particle is about 4.3 minutes, for radium itself 2250 years, while in the case of a very slowly changing element like uranium the average life is of the order of 7000 million years.

It is known that the α -particles from a given element are all shot out with the same speed, but that this speed varies from element to element. There is apparently a close connection between the velocity of ejection of the α -particle and the average life of the parent element. The shorter the average life of the element, the swifter is the speed of expulsion. This interesting relation between the violence of the explosion and the average life of the element holds in the majority of cases, but it is difficult at present to be at all clear of its underlying meaning. Sir William Bragg long ago showed that the α -particle travels through matter nearly in a straight line, and has a definite range of travel in a substance. This is well illustrated by the tracks of α -particles obtained by Wilson's expansion method. The majority of the tracks are seen to be quite straight, apart from an occasional deflection near the end of the path. At the end of the range the photographic and ionising effects of the α -particle apparently cease with great suddenness. On account of its great energy of motion, the individual α -particle can be detected by the scintillation it produces in crystalline zinc sulphide, by the effect on a photographic plate, and by special electrical methods, while the beautiful expansion method of Wilson shows the trail of each individual α -particle through the gas.

We are enabled, particularly by the scintillation method, to count the individual particles, and thus we have at our command a method of great delicacy for studying the effects produced by the passage of α -particles through matter. In travelling through a gas the α -particle passes the outer electronic structure of a large number of atoms and liberates electrons, thus giving rise to an intense ionisation along the track. The ionisation increases to a maximum near the end of the path of the α -particle and then falls rapidly to zero.

A careful study has been made of the law of decrease of velocity of the α -particle in passing through matter by studying the deflection in a magnetic field of a pencil of α -particles before and after its passage through a known thickness of matter. In most of these experiments we employ the α -particles of radium C, which have a range of about 7 cm. in air under ordinary conditions. The initial velocity V_0 of these particles is known to be 19,200 kilometres per second, and the reduction of velocity can readily be followed down to about $0.4 V_0$. At this stage the emergent range of the α -particles is less than one centimetre, and measurements are difficult, owing to the fact that a beam of α -particles becomes heterogeneous and contains particles moving with different velocities.

For this reason the velocity of the α -particle cannot be followed with certainty below $0.38 V_0$. We must bear in mind that even at the lowest velocity at which it is possible to detect the α -particle by the scintillation or photographic method, it is still moving at a high speed compared with the positively charged particles generated in an ordinary discharge tube.

It is clear that ultimately the α -particle must be slowed down to such an extent that it captures electrons and becomes a neutral atom, but until recently no evidence of this process of capture of electrons had been obtained. G. H. Henderson * has recently added much to our knowledge of this subject by examining the deflection of α -rays in a magnetic field in a very good vacuum. For the success of these experiments it is essential that the apparatus in which the deflection is observed should be exhausted to a very low pressure, corresponding to that required for a good X-ray tube. The reason of this will be seen later. When a narrow pencil of α -rays was deflected in a magnetic field two bands were observed on the photographic plate: one the main band, due to ordinary α -particles carrying two positive charges, and another midway band, which he supposed to consist of

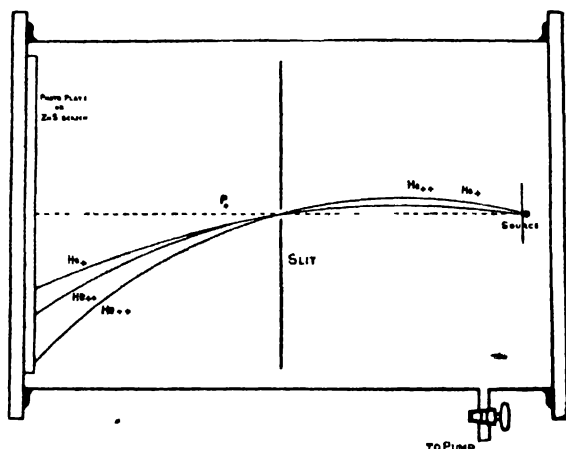


FIG. 1.

particles which had captured one electron, i.e. to singly charged helium atoms. At low velocities he also obtained evidence of the existence of neutral α -particles resulting from the capture of two electrons by the helium nucleus. In these experiments Henderson employed Schumann plates, where the film is so thin that low velocity particles produce as much or more photographic effect than the swifter particles.

I have repeated these experiments by the scintillation method, and confirmed the deduction of Henderson. By observing the deflection of the midway band in an electric as well as in a magnetic field, I find there is no doubt the particles composing the midway band consist of particles of mass 4 and charge 1—i.e. to singly

* Proc. Roy. Soc., A, cii., p. 496, 1922.

charged helium atoms which have the same speed as the doubly charged particles comprising the main band.

Some recent experiments have been made by me to throw light on the conditions under which the flying α -particles may gain or lose an electron. The general arrangement of the experiment is shown in Fig. 1. A fine platinum wire coated with radium B + C, by exposure to the emanation (radon), serves as a nearly homogeneous source of α -rays, since the α -particles are emitted only from the atoms of radium C, which are too few in number to form a film on the platinum of even one molecule thick. The α -rays from this source pass through a narrow slit about 0.3 mm. wide and fall on a screen of zinc sulphide. The distribution of α -particles on the screen is determined by the scintillation method in a dark room, using a microscope outside the box. The vessel containing the source and

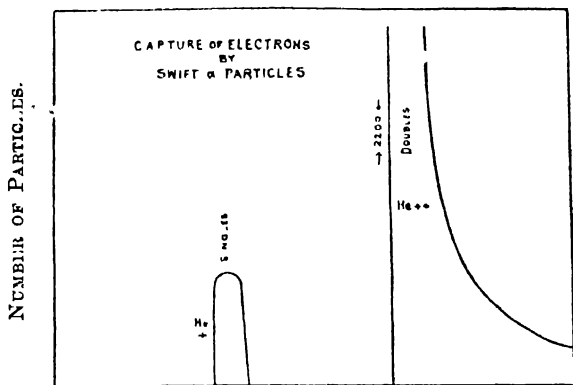


FIG. 2. —DEFLECTION IN MM. BY MAGNETIC FIELD

screen is completely exhausted by means of a Gaede and mercury diffusion pump, and if necessary the residual pressure can be measured by a Macleod gauge. The box is placed between the plane pole pieces of a large electromagnet so that the pencil of α -rays is bent in the direction shown in the figure. Usually the distance between the source and screen was 16 cm., with the slit midway. The whole path of the rays was exposed to a nearly uniform magnetic field, and the deflection of the pencil of rays was proportional to the strength of the magnetic field. Under normal experimental conditions the pencil of α -rays from the bare radium C wire was bent a distance on the screen of about 15 mm. from the zero position without field. The field of view of the microscope was sufficient to take in the depth of the whole pencil of α -rays without the field.

Special precautions were taken to prevent contamination of the screen by the escape of active matter from the wire in a low vacuum. It must be borne in mind that the type of wire source employed always introduces some heterogeneity in the beam of α -rays even from the uncovered source. This is due to the escape from the back of the wire of α -particles which are reduced in velocity in passing through the material. This effect is clearly manifest when the pencil of α -rays is deflected by a magnetic field; for in addition to the main band of α -rays there is always a distribution of particles extending beyond the main beam. The intensity of this heterogeneous beam at any point is generally less than 1 per cent. of the main beam, and does not seriously interfere with the accuracy of the deductions discussed in this lecture.

In Figs. 2 and 3 are given illustrations of the distribution of singly and doubly charged α -particles along the zinc sulphide screen.

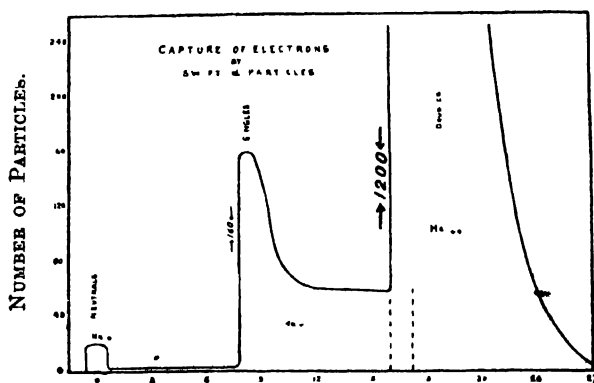


FIG. 3.—DEFLECTION IN MM. BY MAGNETIC FIELD.

Fig. 2 shows the result when a thickness of mica corresponding in stopping power to 3.5 cm. of air is placed over the source. The main band, due to He_{++} particles, is sharply defined on the high velocity side, but there is evidence of some heterogeneity produced in the beam by its passage through the mica. As we should expect, the midway band (He_{+} particles) lies exactly between the zero position and the main band, and contains only about $\frac{1}{8}$ of the particles in the main beam. Fig. 3 shows the distribution when the thickness of mica is increased to correspond to a stopping power of about 6 cm. of air. Both the main and midway bands are no longer sharply defined as in the first case, but each consists of particles with a considerable range of velocities. The relative number of He_{+} and He_{++} particles is about $\frac{1}{8}$ for the swifter particles, but this ratio increases with decreasing velocity. The midway band extends and

joins the main band where it can no longer be followed. The brightness of the scintillations due to He_+ particles falls off obviously and continuously from A to B. At this stage, too, some neutral particles make their appearance. This is shown by the He_0 band, which is not deflected by a magnetic field, but its intensity is small compared with that of the midway band. There is also a sparse distribution of faint particles between the neutral and midway band, probably due in part to scattering of the α -particles by the edges of the slit and possibly in part due to recoil atoms of oxygen and other elements constituting the mica. The distribution of the charged and uncharged helium particles for a still lower velocity will be seen in curves A, B, Fig. 4, which will be referred to later. It is seen that the relative number of He_+ to He_{++} particles has increased; similarly, the relative number of neutral particles is much greater.

We may now consider the interpretation to be placed on these observations. It is clear that the particles emerging from the mica

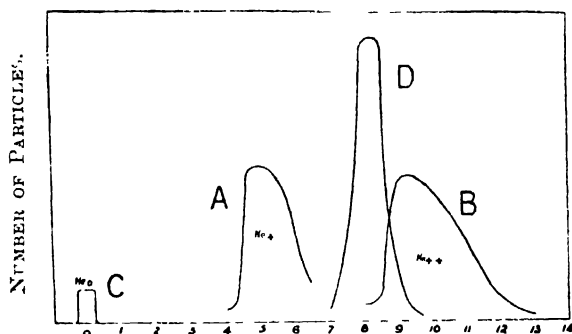


FIG. 4.—DEFLECTION IN MM. BY MAGNETIC FIELD

consist of doubly charged, singly charged, and neutral particles, but the relative number of these three types varies markedly with the stopping power of the mica plate. We may suppose that the α -particle in passing through the outer electron structure of the atoms in its path occasionally removes and captures an electron. This electron falls into a stable orbit round the doubly charged helium nucleus and moves with it.

This singly charged atom will, however, have only a limited life, for in passing through other atoms the electron is knocked off and the singly charged α -particle reverts back to the doubly charged type. This process of removal is analogous to the ordinary process of ionisation where an electron is ejected from an atom by a collision with an α -particle; for as a singly charged particle can remove electrons from another atom, so there is a chance that the He_+ particle

should lose its attendant electron. We may thus consider that two opposing processes are at work, one resulting in the capture of an electron and the other leading to its removal. From the data given later it will be seen that this process of capture and loss may repeat itself more than a thousand times in the flight of an α -particle, so that the average path travelled by an α -particle before capture of an electron or before loss of the captured electron is small compared with the total distance of travel of the α -particle before it comes to rest. It is clear from this, for a given velocity of α -particle, that there must be a momentary equilibrium between the number of He_+ and He_{++} particles such that, on the average, the number of captures in a given small distance is equal to the number of losses.

It is very convenient to suppose that for a given velocity each He_{++} particle has a mean free path λ_1 cm. in the material before it captures an electron, and the He_+ particle a mean free path λ_2 cm. before it loses its attendant electron. No doubt some of the individual particles travel distances much shorter or longer than this mean distance before either capture or loss, but in considering a large number of particles we may suppose there is an average distance traversed before capture or loss, to be called the mean free path.

When N_1 He_{++} particles traverse a small distance dx of a material the number which capture electrons is $N_1 dx / \lambda_1$. If N_2 He_+ particles are present the number which lose an electron is $N_2 dx / \lambda_2$. But we have seen that when an equilibrium is set up, the number of captures in a given distance must equal the number of losses. Equating these two expressions, it is seen that $N_2 / N_1 = \lambda_2 / \lambda_1$, or, in other words, the relative number of He_+ to He_{++} particles is proportional to the ratio of the mean free path for loss to that for capture. Since by the scintillation method the ratio N_2 / N_1 can be measured for any velocity, by using different thicknesses of absorber we can thus determine the ratio of the mean free paths for capture and loss for any velocity.

The actual value of the mean free path λ_2 of the He_+ particle before it loses its electron can be directly determined by experiment. Suppose the microscope is focussed on the midway band of Fig. 2 and the number of scintillations per minute observed in a good vacuum. If the pumps are shut off and a small quantity of air or other gas is introduced into the apparatus, the number of scintillations is found to diminish with increasing pressure of the air until the band has completely disappeared. This takes place at quite a low pressure of air: for example, for a pressure of about 1/4 mm. in the box.

The explanation of this result is obvious. The He_+ particles which escape from the mica occasionally collide with an atom of the gas in its path, and the electron which it captured in passing through the mica is removed. In such a case the He_+ becomes again an

He_{++} particle, and the latter is twice as easily deflected in a magnetic field as the former. Suppose the collision occurs for the first time at the point P (Fig. 1). The particle after losing its electron travels along a new path shown in the figure, and the particle no longer strikes the part of the screen viewed by the microscope. It is found that the number of scintillations seen in the microscope falls off according to an exponential law as the pressure of the gas is raised. Such a result is to be expected, and from this data the average distance which the He_{+} particle traverses before it loses its electron can be simply deduced. Certain small corrections are necessary to take into account the finite width of the band of scintillations as seen in the microscope, but we need not enter into details at this stage. It is convenient to express the mean free path λ_2 in air of the He_{+} particles, not as the average length of path traversed in the rarefied gas before loss, but as the distance traversed in the same gas at standard pressure and temperature. For example, in a certain experiment the mean free path in air of the particle was found to be 12 cm. at a pressure of 0.040 mm.; this corresponds to a mean free path of 0.0063 mm. at standard pressure and temperature.

In this way the mean free path in air before loss of an electron has been measured for different velocities, and it has been found over a considerable range that the mean free path varies directly as the velocity of the α -particle, so that the mean free path becomes shorter as the velocity of the α -particle diminishes. Since we may regard the loss of an electron from the singly charged particle as the result of a process of ionisation, such a relation is to be expected, and indeed, if we take into account the strong binding of a single electron by the He_{++} nucleus, the mean free path for loss is of the same order as that calculated from considerations of the number of ions per cm. produced by the α -particle in air and other gases. Comparisons have been made of the mean free path in air with that in hydrogen and helium. Its value is 4 to 5 times longer in hydrogen and more than 5 times longer in helium.

Now that the mean free path λ_2 is known, the value of λ_1 for capture can be deduced if the ratio N_2/N_1 is also known. A difficulty, however, arises at this point. In order to measure the ratio N_2/N_1 it is necessary that the active source should be covered with mica or other solid material. Gas cannot be used conveniently. It was found, however, that the ratio N_2/N_1 was the same within the limits of error whether the α -particles were reduced in velocity by passage through celluloid, mica, aluminium, or silver. For this purpose the mica was kept the same and a very thin sheet of the substance under examination spread over it. The thickness of the sheet was sufficient to set up a new equilibrium between the singly and doubly charged particles, but not sufficient to alter materially the velocity of the ionising rays.

Since the value of the ratio N_2/N_1 suffers no appreciable change

for absorbers of such different atomic weights, we may safely conclude that the ratio for a hypothetical sheet of solid air would be the same as for mica.

We have now all the data required to determine the values of λ_1 and λ_2 corresponding to α -particles of different velocities. The results are given in the following table for three different velocities. The mean free paths are expressed in terms of millimetres of air at standard pressure and temperature. V_0 , the maximum velocity of the α -particles from radium C, is 1.9×10^9 cm. per second.

Velocity V in terms of V_0	$\lambda_2/\lambda_1 = N_2/N_1$ for Mica	Mean Free Path λ_2 for Loss in Air	Mean Free Path λ_1 for Capture in Air
0.94	1.200	0.011 mm.	2.2 mm.
0.76	1.67	0.0078 mm	0.52 mm
0.47	1.75	0.0050 mm	0.037 mm

It has been seen that the mean free path for loss varies directly as the velocity, and thus only alters in a ratio of about 1 to 2 over the range of velocities given in the table. On the other hand, the ratio λ_2/λ_1 increases very rapidly with diminution of velocity varying approximately as V^{-1} . From this it follows that λ_1 varies as V^2 , thus decreasing by a factor of 60 or more when the velocity is halved.

From these data and relations it can easily be calculated that the mean free path for capture should be equal to that for loss for a velocity about $0.3 V_0$, and for this speed the numbers of He_+ and He_{++} particles should be equal.

The actual value of the velocity for equality of the two types in a special experiment was found to be $0.29 V_0$, in good agreement with the calculated value. It is a difficult matter to determine the values of λ_1 and λ_2 for velocities less than $0.3 V_0$, for not only are the scintillations weak in intensity and difficult to count with accuracy, but also the issuing rays are very heterogeneous and no longer show well-defined edges on the high velocity side. It was, however, noted that the ratio N_2/N_1 rapidly increased below the velocity $0.3 V_0$.

We have so far dealt with the equilibrium between He_+ and He_{++} particles. It is clear, however, that similar considerations apply to the equilibrium between singly charged and neutral helium particles at low velocities of the α -particle. It was noted that the neutral particles appear prominently after the rays have passed through mica of 6 cm. stopping power, but no doubt they could be detected for still lower stopping power. These neutral particles, of course, produce scintillations, but of an intensity corresponding to an α -particle of low velocity. These neutral particles probably lose and regain an electron many times before they are stopped in the

zinc sulphide or other absorbing material. This effect was shown by introducing gas at low pressure into the apparatus, when the scintillations due to the neutral particles diminished in number and ultimately vanished. The explanation of this is similar to that given for the disappearance of the He_+ band, for the neutral particles occasionally lose an electron in passing through the gas and are then deflected away from the zero position by the magnetic field.

It was estimated that the mean free path in air for conversion of neutral helium particles to singly charged particles was about $1/600$ mm. No doubt this is an average for particles of very different velocities which may be present in the neutral band.

For the higher velocities we have to deal mainly with the interchange $\text{He}_{++} \rightleftharpoons \text{He}_+$. For velocities less than $0.5 V_0$ the interchange $\text{He}_+ \rightleftharpoons \text{He}_0$ also comes in and becomes all-important for velocities less than $0.3 V_0$. No doubt, as Henderson has shown, at still lower velocities most of the He_{++} particles disappear and the He_0 and He_+ particles predominate.

At these low velocities counting scintillations becomes very difficult and uncertain, and the photographic method, as used by Henderson, is preferable. It will be a matter of very great interest to examine whether the relative numbers of the three types of particles alter when the α -particles are slowed down by passage through different materials. This side of the work is being attacked by Mr. Henderson in the University of Saskatchewan.

There is one very interesting point that may be considered here. It has been shown that these singly and doubly charged α -particles are always present after the α -rays have passed through mica or other absorber: but are there any singly charged particles present when α -particles escape from a wire coated with an infinitely thin deposit of active matter? This was first tested for a platinum wire coated with a deposit of radium B + C by exposure to the radium emanation, when it was found that singly charged helium atoms were present in about the equilibrium ratio for this velocity. This was a rather surprising observation, but it was thought it might result from the fact that by the recoil from radium A the radium B particles penetrate some distance into the material of the wire. Under these conditions many of the α -particles expelled from radium C have to pass through a small but appreciable thickness of matter before escape from the wire, and might thus capture electrons. This explanation seemed unlikely because the average distance penetrated by the recoil atom is only a minute fraction of the mean free path for capture at such high velocities of the α -particle. The experiment was tried with a nickel wire on which radium C had been deposited on the surface by the well-known method of dipping the wire in a hot solution of radium C. In this case the difficulty due to recoil is absent, but the number of singly charged particles was the same as before.

It is very significant that the relative number of singly and doubly charged particles is about the equilibrium ratio to be expected when the wire, after being activated, is coated with an appreciable thickness of copper or other material. We can scarcely suppose that singly as well as doubly charged particles are actually liberated from the radioactive nucleus itself, for even if it be supposed that an α -particle with an attendant electron is expelled, the electron must be removed in escaping through the very powerful electric field close to the nucleus. It is much more probable that the doubly charged α -particle in passing through the dense distribution of electrons surrounding the radioactive nucleus occasionally captures an electron, and that the process of capture and loss goes on to some extent in escaping from the radioactive atom. This seems at first sight rather unlikely when we consider the relatively large number of atoms an α -particle ordinarily passes through before equilibrium between capture and loss is established, but it is well known that the chance of effective electronic collisions appears in general to be greater for a charged particle expelled from the central nucleus than for a similar particle passing from outside through the electronic distribution of an atom. It may be that those electrons the orbital motion of which round the nucleus is comparable with the speed of the α -particle are particularly effective in causing capture or loss.

So far we have dealt mainly with the distribution in a magnetic field of the particles in a vacuum after their escape from a mica surface. Some very interesting points arise when the distribution is examined in the presence of sufficient gas to cause a rapid interchange of capture and loss along the path of the α -particle in the gas. This is best illustrated by a diagram, Fig. 4, in which the results are given for α particles escaping through mica with a maximum emergent range of about 4 or 5 millimetres in air. Curves A and B give approximately to scale the distribution of He_+ and He_{++} particles in a vacuum, while C gives the relative number of neutral particles under the experimental conditions. Suppose now sufficient air is introduced into the vessel to cause many captures along the gas, but yet not enough to reduce seriously the velocity of the α -particles. The first salient fact to notice is that the distributions A, B, C vanish and there remains a distribution of particles (curve D) about midway between A and B. This band is narrower than either A or C, and its height at the maximum much greater than either. It is evident that the particles have been compressed into a band of much narrower width than the normal distribution in curve B.

This is exactly what we should expect to happen. The swifter particles present suffer less capture than the slow; consequently the average charge of the swifter α -particles along the gas is less than $2e$, and their deflection is less than the swiftest particles shown in

curve B. On the other hand, the slower α -particles have an average charge nearer $1e$ than $2e$, and are relatively still less deflected than the swifter particles. It is thus clear that the resulting distribution of particles with air inside the vessel will be concentrated over a much narrower width than the main band of He_{++} particles. From calculation based on the laws of capture and loss, the width of the band under the experimental conditions can be deduced, and is found to be in good accord with experiment. It will be seen to be significant that similar results have been observed for hydrogen under corresponding conditions.

GENERAL DISCUSSION OF RESULTS.

Attention may now be devoted to a consideration of the results so far obtained and the possibility of their explanation on present views. In the first place, it is important to emphasize the large number of capture and losses that occur during the flight of an α -particle from radium C. While the mean free path of the α -particle from radium C of 7 cm. range is about 3 mm. in air, its value rapidly decreases with lowering of the velocity of the α -particle, and is probably about 0.0015 mm. for a velocity of $0.3 V_0$. It is not difficult to calculate that not far short of a thousand interchanges of charge occur during the path in air of a single particle between velocities V_0 and $0.3 V_0$. While the data so far obtained do not allow us to calculate the number of interchanges of charge that occur between velocities $0.3 V_0$ and 0, it seems probable that the number is considerably greater than a thousand. We have already pointed out that for low velocities the interchange $\text{He}_+ \rightleftharpoons \text{He}_0$ predominates. When we consider the rapidity of interchange of charges of the α -particle at average velocities, it seems clear that we cannot expect to observe any appreciable difference in power of penetration between a beam of rays of the same velocity, whether consisting initially of singly or doubly charged particles. It is clear that a singly charged particle after penetrating a short distance is converted into a doubly charged particle, and vice versa, and that the effects due to the two beams should be indistinguishable. Henderson tried such absorption experiments, using the photographic method, but with indefinite results.

When an α -particle captures an electron, the latter presumably falls into the same orbit round the helium nucleus as that which characterises an ionised helium atom, i.e. an atom which has lost one electron. When the α -particle with its attendant electron passes swiftly through the atoms of the gas in its path, it will not only ionise the gas but will also occasionally be itself ionised, i.e. will lose its attendant electron. When we take into account the strong binding of the first electron to the helium nucleus—ionisation potential about 54 volts—the mean free path for loss of the captured

electrons in air is of the right order of magnitude to be expected from considerations based on the ionisation by the α -particle per unit path in air. While we can thus offer a quantitative explanation of the mean free path for loss observed experimentally, the inverse problem of the capture of an electron by the flying α -particle presents very great difficulties.

In the actual case, the α -particle is shot at high speed through gas molecules which for all practical purposes may be supposed to be at rest. For convenience of discussion, however, it is preferable to make an equivalent assumption — namely, that the α -particle is at rest and the gas molecules stream by it with a velocity equal and opposite to that of the α -particle. Now the maximum velocity of an α -particle from radium C is equivalent to that gained by an electron in falling freely between a difference of potential of about 1000 volts; so that the electrons comprising the molecules of air or other gas have a velocity of translation numerically equal to this. For brevity, it is very convenient to speak of this velocity or energy as that due to a "1000-volt" electron.

When the electrons in an atom pass close to the α -particle, one of them may be removed from the parent atom by the collision, energy being required for this process. The ionisation potential for oxygen or nitrogen is about 17 volts, which is a very small quantity compared with the energy of translation of a 1000-volt electron.

If we consider the forces involved between an α -particle and moving electron as of the ordinary electrostatic type, the electron will describe a hyperbolic orbit round the nucleus, the angle of deflection of the path of the electron resulting from the collision depending on the nearness of the approach of the electron to the nucleus. On ordinary dynamics, the electron will never be captured in such a collision if there is no loss of energy by radiation. If capture for some reason results from the collision, it means that an amount of energy corresponding to at least a 1000-volt electron has in some way been got rid of. This loss of energy may be supposed to be due to some interaction between the α -particle and colliding nucleus with its attendant electrons, or to the loss of energy by radiation during the collision. The first supposition seems at first sight plausible, for we know that the innermost electrons of oxygen or nitrogen are strongly bound and require energy of the order of 500 volts to remove them from the atom. But there is one very strong and, it seems to me, insuperable objection to this view.

I have found that the deflection in a magnetic field of a pencil of α -particles passing through a suitable pressure of hydrogen is similar to that shown in curve D, Fig. 4, for air. This shows that the α -particle passing through hydrogen captures electrons of energy about 120 volts to about the same degree as in air. Now we know that the electrons in the hydrogen atom or molecule are lightly bound, and an energy of not more than a 30-volt electron, suitably

applied, would entirely separate the component nuclei and electrons in the hydrogen molecule. In the case of hydrogen, therefore, we cannot hope to account for the requisite loss of energy, which for the experiment considered is about 100 volts. If these experiments with hydrogen are correct, and are valid for all velocities of the α -particle, we are driven to conclude either that some unknown factors are involved in the capture, or that the loss of energy of the electron must be ascribed to radiation. In such a case capture of an electron may be regarded as the converse of the photo-electric effect, where radiation falls on matter and swift electrons are ejected from the matter. In the case under consideration swift electrons are shot towards a charged nucleus and an occasional electron is captured with the emission of energy in the form of radiation. On such an hypothesis the radiation of energy from an α -particle passing through a gas due to the frequency of capture is very great, amounting to about 3 per cent. of the total energy of the α -particle. This seems to be an unexpectedly large amount, but cannot be ruled out as impossible in the present state of our knowledge.

In the discussion of this very thorny question, I have confined myself mainly to the case of capture by the swift α -particle, where the difficulties of explanation are much greater than for capture at slower velocities. Our information is at present too incomplete to give a decisive answer, but there seems to be no doubt that the unexpected frequency of capture of electrons by swift α -particles raises many new and interesting questions of the nature of the processes that can occur in collisions between electrons and matter.

I need scarcely say that the phenomena of capture and loss are not confined to the α -particle, but are shown by all charged atoms in swift motion through a gas, and were long ago observed in the case of positive rays. On account, however, of the high velocity of the α -particles and the ease of their individual detection, the process of capture and loss can be studied quantitatively under simpler and more definite conditions than in the case of the electric discharge through a gas at low pressure.

On this occasion I have devoted my attention to the most recent additions to our knowledge of the life history of the α -particle. This knowledge has been obtained from the study of the rapid interchange of charges when an α -particle passes through matter. I have only incidentally referred to the numerous collisions with electrons along the track of the α -particle which result in dense ionisation. I have omitted any consideration of those rare but interesting encounters in which an α -particle is deflected through a large angle by a close collision with a nucleus. I have omitted, too, the still rarer encounters that may result in a disintegration of an atomic nucleus like that of nitrogen or of aluminium. We have seen that an α -particle has an interesting history. Usually it is retained as an integral and orderly part of a radioactive nucleus for an interval of

more than a thousand million years. Then follows a cataclysm in the radioactive nucleus; the α -particle gains its freedom and lives an independent life of about one hundred millionth of a second, during which all the incidents referred to in this lecture occur.

If we are dealing with a dense and compact uranium or thorium mineral, the α -particle after acquiring two electrons and becoming a neutral helium atom may be imprisoned in the mineral as long as the mineral exists. The occluded helium can be released from the mineral by the action of high temperature, and after removal of all other gases can be made to show its presence by the characteristic brilliant luminosity under the stimulus of the electric discharge. In the circumstances of such an experiment only small quantities of helium are liberated. Large quantities of helium, sufficient to fill a large airship, have, however, been isolated from the natural gases which escape so freely from the earth in various parts of Canada and the United States. It is a striking fact that every single atom of this material has in all probability had the life history here described.

ADDENDUM.*

It may be of interest to give here a brief review of some additional facts in connection with the α -particle, brought to light in recent years. It has long been known that α -particles, although projected from the source at the same speed, travel unequal distances through a gas. For example, the maximum distance travelled by the α -particles from radium C in air is 7.04 cm. at 760 mm. and 15° C., the minimum distance is about 6.4 cm., and the mean distance about 6.8 cm. Some "straggling" of the α -particles is to be anticipated on general grounds, since the α -particle loses its energy mainly in liberating electrons from the atoms of matter in its path. On the laws of probability one α -particle may meet more atoms and liberate more electrons than another, and thus lose energy at a faster rate. The amount of straggling observed is, however, much greater than can be accounted for in this way, and the occasional large deflections of the α -particles due to nuclear collisions are so rare, except near the end of the range, that they do not seriously influence the final distribution.

Henderson has suggested that the property of an α -particle of capturing and losing electrons will introduce a new factor in causing straggling. No doubt this is the case, but the rates of capture and loss observed appear to be too rapid to account entirely for the discrepancy between theory and experiment. Another interesting suggestion has been made by Kapitza to account for the magnitude of this straggling. From the experiments of Chadwick and Bieler

* This did not form part of the Discourse, but it may usefully supplement one or two of the points surveyed in the lecture.

on the collision between α -particles and hydrogen nuclei, it has been deduced that the α -particle or helium nucleus has an asymmetrical field of force around it. This asymmetry of the electric field must become small at the distance of the orbits of the electrons in the neutral helium atom, but may be sufficient to fix the plane of the orbit of an electron relative to the axis of the helium nucleus.

Suppose that the α -particles liberated from a radioactive source have their axis orientated at random, and that the direction of the axis of each individual particle remains unchanged during its motion. In some cases, for example, the captured electron will describe an orbit of which the plane is nearly in the direction of motion of the α -particle; in other cases nearly perpendicular to it. It is to be expected, however, that the chance of losing the captured electron by collision will be greater in one case than the other; or, in other words, the mean free path of the singly charged α -particle before loss of its electron will be different in the two cases.

On this view it is to be anticipated that one group of α -particles will lose energy faster than the other, and the ranges will be different. In order to test whether α -particles show the individual differences to be expected on this theory, Kapitza has photographed in the Cavendish Laboratory the tracks of a number of α -particles by the Wilson expansion method, using a strong magnetic field of about 70,000 Gauss, produced by a momentary current of great intensity. The magnetic field was sufficiently strong to cause a marked bending of the track of the α -particle. It was found that the curvature of the tracks at equal distances from the ends showed marked variations. Before any definite decision can be reached a large number of tracks obtained in this way must be carefully measured up and allowance made for the sudden bends which occur due to a nuclear collision with the atoms of nitrogen or oxygen. The frequency of these bends near the end of the range complicates the interpretation of the apparent curvature which is measured. The experiments, which are still in progress, are difficult and require great technical skill, and it will be a matter of much interest if any definite asymmetry in the orbits of the singly charged α -particles can be established by this or other methods. If such an asymmetry exists, it must influence to a small extent the arrangement of the two electrons round the helium nucleus and possibly their spectrum.

During the past two years Blackett, in the Cavendish Laboratory, has made a careful examination of the frequency of occurrence of sharp bends or forks in the tracks of α -particles near the end of their range in air and other gases. For this purpose a simple form of Wilson expansion chamber, of the type designed by Shimizu, has been used, and each track has been photographed in two directions at right angles to each other to fix the angle of the forks in space. A large number of photographs have been taken, and the frequency of the forks has been examined in different gases, particularly in the

last centimetre of the range of the α -particle. Assuming that these forks arise from nuclear collisions, it is possible to deduce from the experimental data the variation of velocity of the α -particle near the end of its range. It is known from the work of Geiger and Marsden that the maximum velocity v of the α -particles of emergent range R is given by $v^2 \propto R$, when R is not less than one centimetre. Blackett finds that this relation between velocity and range no longer holds near the end of the track, but is replaced by a relation of the form $v^{1.5} \propto R$.

In the course of these experiments a number of well-defined forks have been photographed in hydrogen, helium, air and argon by Blackett, and also by Auger and Perrin in Paris. By measuring the angles between the original direction of the α -particle and the direction of the colliding particles after collision, the accuracy of the laws of impact can be directly tested. The results are found, within experimental error, to be in agreement with the view that the impacts are perfectly elastic, and that the conservation of energy and of momentum hold in these nuclear collisions. Conversely, by assuming that the impacts are perfectly elastic, it is possible to deduce the mass of the recoil atom in terms of the α -particle of mass 4.00. For example, a fork in helium gave the mass of the recoil atom 4.03, and a fork in hydrogen gave the mass of the recoil atom 1.024. In a collision between the α -particle and a helium nucleus the angle between the forks should be exactly a right angle; the value measured was $89^\circ 45'$.

[E. R.]

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